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Chemical Characterization and
Toxicologic Evaluation of
Airborne Mixtures

Chemical Characterization of
Colored Signal Smokes

Final Report

December 1988

M. V. Buchanan
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CHEMICAL CHARACTERIZATION AND TOXICOLOGIC
EVALUATION OF AIRBORNE MIXTURES

CHEMICAL CHARACTERIZATION OF COLORED SIGNAL SMOKES

M. V. Buchanan and C. Y. Ma

Analytical Chemistry Division
Oak Ridge National Laboratory

DECEMBER 1988



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EXECUTIVE SUMMARY

The chemical compositions of four colored smoke mixes, red, violet, green, and yellow have been characterized to assess possible changes in composition due to the combustion of these materials as smoke grenades. Smoke mixes which were from the same lots as those used in the fabrication of the smoke grenades were first fractionated by high performance liquid chromatography or open column liquid chromatography. These materials were then characterized using mass spectrometry, including combined gas chromatography/mass spectrometry, direct probe low resolution mass spectrometry, and laser desorption Fourier transform mass spectrometry, to provide tentative identifications. More confident identities were assigned to major components using supporting spectroscopic data, primarily carbon-13 nuclear magnetic resonance and Fourier transform infrared spectroscopy, and by comparing chromatographic retention times with authentic standards.

In order to generate and collect combusted dye materials, smoke grenades were detonated in family-sized camping tents, which served as combustion and sampling chambers and prevented escape of the smoke into the environment. Both particulate and vapor phase constituents were collected for chemical characterization using a variety of traps and filters. In addition, samples for particle size distribution were obtained on a cascade impactor.

The organic components from the combusted particulates were chromatographically isolated and spectroscopically characterized in a manner similar to the original smoke mixes. Vapor phase samples collected on Tenax and XAD-2 resin traps were analyzed by combined gas chromatography/mass spectrometry after either thermal desorption or extraction from the resin.

The combustion of the green, yellow and violet grenades produced characteristically colored smokes. The red grenades (nine tested from two different lots) only produced small amounts of a grayish smoke after substantial flaming. Further, the particulate matter collected from the red grenades was a very dark, oily substance. This material was chemically characterized and is reported. However, a red grenade from a third lot was detonated and did produce a "normal" red smoke. The products from this red grenade were also characterized and found to be qualitatively (although not quantitatively) similar to the "abnormal" grenades. In all of the grenades studied, the major components of the combusted particulates were the unaltered original dyes. The red and the violet smoke mixes appeared to undergo more chemical transformation than the green and yellow smoke mixes. Two of the components in the combusted violet smoke mix, aminoanthraquinone and 1,4-diaminoanthraquinone, have been previously shown to exhibit bacterial mutagenicity, although these compounds were produced at relatively low levels (< 5% relative to the major component). Other aminoanthraquinone-based products were also observed in the violet smoke mix.

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INTRODUCTION

The U.S. Army uses colored smokes from M18 smoke grenades for signalling and marking. Previous studies (1,2) of colored smoke dyes used in these grenades have shown that some dye materials are transformed in the combustion process to yield different chemical species, some of which exhibit biological activity. For example, in a previously studied violet grenade, the major component, 1,4-diamino-2,3-dihydroanthraquinone, was effectively converted to a mutagenic compound, 1,4-diaminoanthraquinone, during the combustion process (1,5). To avoid potential health effects from these types of smokes, four new candidate dye mixtures, including red, yellow, green, and violet, have been developed. In this study, these four new smoke mixes have been chemically characterized both before and after combustion as M18 smoke grenades in order to evaluate chemical changes which might occur.

The first part of this study involved the characterization of the five organic dyes used in the formulation of the four smoke grenades. Standards of these five dyes ("dye standards"), as well as samples of the dye materials actually used in the fabrication of the grenades ("smoke mixes") for the combustion studies were supplied by the U.S. Army Chemical Research, Development and Engineering Center (USACRDEC), Aberdeen Proving Ground, MD, through the sponsor, the U.S. Army Biomedical Research and Development Laboratory (USABRDL). The characterization of the dye standards and the smoke mixes was accomplished using separation and identification techniques similar to those which were successfully employed in previous studies (1-5) in these laboratories. The major components of each of the dye standards and smoke mixes were separated into fractions prior to obtaining spectroscopic data. Where possible, gas chromatographic (GC) and/or high performance liquid chromatographic (HPLC) profiles of the fractions from the uncombusted materials were obtained for comparison with similar fractions isolated from the combusted smoke mixes. Spectroscopic techniques, such as infrared (FTIR), ^{13}C nuclear magnetic resonance (NMR), ultraviolet/visible (UV-VIS), and mass spectrometry (MS), were used to establish the identity of the major components (> 1% by chromatographic area) present in the dye standards and smoke mixes.

The second part of this study involved two tasks. The first task was the generation and sampling of the combusted smokes, and the second task was the characterization of both the particulate and volatile components from the combusted smoke. Detailed descriptions of the smoke generation and sampling protocols are contained in this report. It also contains information on the fractionation procedures, chemical characterization of major components (both volatiles and particulates), and the average particle size of the smoke aerosols.

MATERIALS AND METHODS

Dye Standards and Smoke Mixes

Five dye standards were supplied by the USACRDEC. Information on the chemical structures of these five dye standards are given below:

Solvent Red 1: Color Index (CI) 12150; Chemical Abstract Registry Number (CAS) No. 1229-55-6; α -methoxybenzenazo- β -naphthol ($C_{17}H_{14}N_2O_2$); (MBN, Fig. 1, I) (Lot No. 30100-21)

Disperse Red 11: CI 62015; CAS No. 2872-48-2; 1,4-diamino-2-methoxy-9,10-anthraquinone ($C_{15}H_{12}N_2O_3$); (DMA, Fig. 1, II) (Lot No. 31195-057)

Disperse Blue 3: CI 61505; CAS No. 2475-46-9; 1-[(2-hydroxyethyl)-amino]-4-(methylamino)-9,10-anthraquinone($C_{17}H_{16}N_2O_3$); (HEMA, Fig. 1, III) (Lot No. 62-611)

Solvent Green 3: CI 61565; CAS No. 128-80-3; 1,4-di-p-toluidino-9,10-anthraquinone ($C_{28}H_{22}N_2O_2$); (PTA, Fig. 1, IV) (No Lot number designated)

Chinoline Yellow (also Solvent Yellow 33, Quinoline Yellow): CI 47000; CAS No. 83-08-9; 2-(2'-quinolinyl)-1,3-indandione ($C_{18}H_{11}NO_2$); (QID, Fig. 1, V) (Lot No. 13030-006)

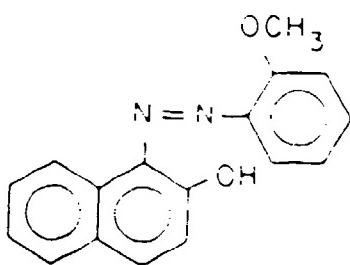
In addition, several dye standards were purchased from commercial sources to assess possible purification, fractionation and identification techniques prior to receipt of the dye samples and smoke mixes from USABRDL. Solvent Red 1 was obtained from Tokyo Kasai Kogya Co. (Tokyo, Japan); Disperse Red 11 from Sigma Chemical Co. (St. Louis, MO); Disperse Blue 3 and Disperse Blue 14 (CAS 2475-44-7, CI 61500, 1,4-bis(methylamino)-anthraquinone) from Aldrich Chemical Co. (Milwaukee, WI).

Samples of the five smoke dye mixes actually used in the formulation of the four colored smoke grenades employed in this study, were obtained from Pine Bluff Arsenal (Pine Bluff, Arkansas), and are referred to in this report as Smoke Mixes:

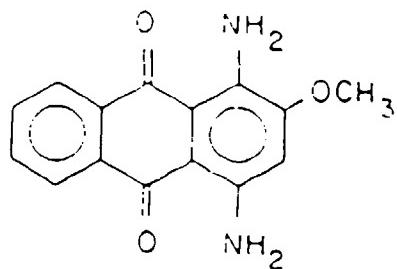
Green Smoke VII, 6820-00N00-0019, Lot #RJC-83K-003
Solvent Yellow 33, 6820-00-M00-0019, Lot #THF-11-49
Disperse Red 11, 6820-00-M00-0023, Lot #01195-001
Solvent Red 1, No FSN, Lot #30100-23
Disperse Blue 3, No FSN, Lot #50038-001

Combustion and Sampling

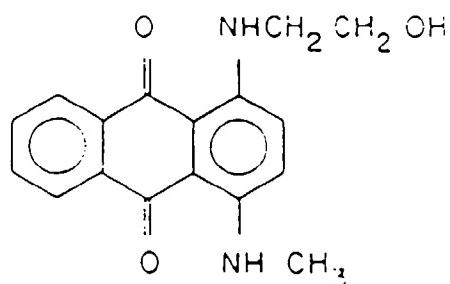
Previous studies (1,5) have proven the utility of employing tents as combustion and sampling chambers for colored smoke grenades. The tents



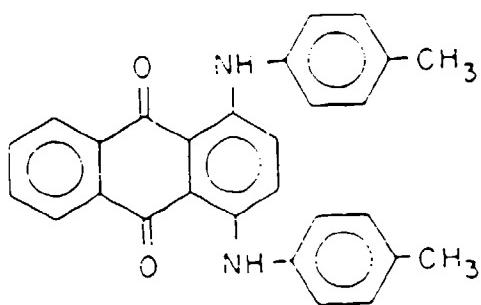
I. SOLVENT RED 1
MBN



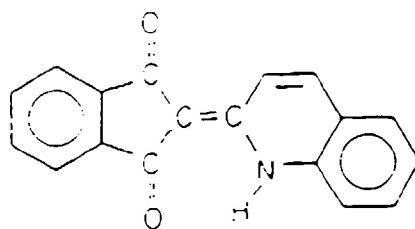
II. DISPERSE RED 11
DMA



III. DISPERSE BLUE 3
HEMA



IV. SOLVENT GREEN 3
PTA



V. SOLVENT YELLOW 33
QID

Figure 1. Chemical Structures for the Dye Standards

have the advantage of excellent containment of the generated smoke (virtually no observed leaks of the smoke), low cost, and ease of disposal. The experimental setup for these combustion studies was essentially the same as used for the previous combustion studies (1). The colored smoke grenades were detonated in separate tents (9 x 11 x 6-2/3 ft., Sears Roebuck, Catalog No. 6G77105C). The window flaps were taped shut to prevent escape of the smoke into the atmosphere. In the combustion experiments of red smoke grenades, the window openings were covered with clear plastic (sealed with tape) to allow observation of the combustion process.

The smoke grenades were securely clamped over a galvanized tub, which contained about two inches of gravel to prevent ignition of the tent floor material. Aluminum foil was placed on the floor of the tent surrounding the tub as an additional precaution against igniting the tent floor. The grenades were detonated remotely using a pull cord tied to the pin.

Airborne particulate material was collected in a prewashed, cellulose thimble (43 x 123 cm, Whatman, Inc., Clifton, NJ) held in an Anderson stainless steel filtering thimble holder (Anderson Samplers, Inc., Atlanta, GA). Air was pulled through the holder at a rate of 105 L/min by a 1/2 hp Doerr Carbon Vane Pump (Doerr Electric Co., Cedarburg, WI). The sampling thimble was backed up by a ultra filter cartridge (type H, Mine Safety Appliance Co., Pittsburgh, PA) to prevent particulates from entering the pump. Fallout particulates were also collected in six to ten glass trays (30 x 45 cm) placed on the floor of the tent. The combustion process and sampling time lasted for approximately 50 minutes. At test time, the temperature of tent interior was 2 to 5°C higher than the outside temperature. Observed temperature increased inside the tent as a result of the combustion process: from an initial 32.8°C to 36.1°C for the red grenade; from 33.7°C to 41.0°C for the violet grenade; from 21.4°C to 27.2°C for the yellow grenade; and from 22.0°C to 24.0°C for the green grenade.

Vapor phase samples were collected by drawing air through Teflon tubes inserted through slits in the tent walls. To collect volatile and semivolatile materials, glass tubes (10 mm ID x 25 cm) filled with either pretreated Amberlite XAD-2 (Polysciences, Warrington, PA) or Tenax-GC (Applied Science Division, Milton Roy Laboratory, State College, PA) resins (6) were used. A Cambridge fiberglass filter pad was placed in front of the resin traps to exclude particulate material. Two samples were taken on each type of resin during the sampling period, starting at 3 minutes and again at 30 minutes after ignition. Air was drawn through the resin cartridges typically for 10 minutes. Sampling flow rate was 1 liter/min using a Dupont Model P4000 air sampling pump (E. I. Dupont de Nemours Co., Applied Technology Division, Wilmington, DE). Blank air samples were collected on both types of resins immediately prior to each combustion experiment in order to discriminate between the background contaminants and the tent environment.

At each combustion test, a member of the ORNL Fire Department was present in case of an emergency. The entire experimental protocol was reviewed prior to the first combustion test by a member of the ORNL Safety Department to ensure the safety of the process. All tests were conducted without incident. After the tests were completed, the tents were collapsed, folded and sealed in a container for disposal according the ORNL protocols for chemical wastes.

Separations and Chemical Characterization

High Performance Thin Layer Chromatography (TLC). Solutions of the dye mixes were made at concentrations of 2 to 5 mg/mL by dissolving weighed amounts in methylene chloride and high performance silica gels (0.2 mm thickness, Si-F₂₅₄) or alkylamino-bond silica gel TLC plate (precoated TLC plates, NH₂-F₂₅₄-5, 0.2 mm thickness, E. Merck, Darmstadt, West Germany) were spotted with 0.5 or 1.0 μ L of this solution. The samples were spotted 1 cm from the lower edge of the plate, which was then developed in an ascending direction in a presaturated tank. Except as noted in the text, two mobile phases were used: 100% methylene chloride and 50% acetonitrile in methylene chloride. A typical development required approximately 15 minutes for the solvent front to reach 85 mm from the origin. In some instances, reversed phase TLC plates (C₁₈-Plate, 0.2 mm thickness, E. Merck, Darmstadt, West Germany) were also used (elution with 90/10 mixture of methanol and water). Most components separated on the TLC plates were readily visible as characteristic colored spots. Some components, where not visible, were detected as dark blue spots under a 254 nm UV lamp.

High Pressure Liquid Chromatography (HPLC). The semipreparative scale HPLC system consists of the following components: (1) a six part Valco loop injector equipped with a 200 μ L or 20 μ L sample loop (Valco Instrument Co., Houston, TX); (2) a simplex reciprocating pump (Laboratory Data Control Division, Milton Roy Co., Riviera Beach, FL); (3) a pressure gauge (Ashcroft Gauge, Dresser, Inc., Stratford, CT) and (4) an Altex Model 153 UV detector (Altex/Beckman Instruments, Inc., Berkley, CA) equipped with an 8 μ L flow cell and monitoring wavelength of 254 nm. A Partisil-10 polar amino-cyano (PAC) column (1 cm x 25 cm, Whatman, Inc., Clifton, NJ) was used for both semipreparative and analytical scale analyses. The column was preceded by an MPLC® Guard Column (Brownlee Labs, Inc., Santa Clara, CA) equipped with an Amino H1-GU cartridge. Two mobile phases were used: 100% methylene chloride and 30% (V/V) acetonitrile in methylene chloride, at a flow rate of 3 mL/min.

Gas Chromatography (GC). A Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector (FID) was used. The column was a 30 m x 0.24 mm ID fused silica capillary column (J and W Scientific, Folsom, CA) with a bonded liquid phase (DB-5, 0.25 μ m film thickness). For the analysis of the dye standards, smoke mixes, and combusted particulates, the column temperature was initially held at 100° for 10 minutes, then raised to 280°C at a rate of 8°C/min. The column head pressure of the helium carrier gas was set at 16 psi and the air and

hydrogen tank pressures were set at 20 psi and 25 psi, respectively. Both the injector and FID were maintained at 280°C. The GC conditions used for the study of the volatile components collected during combustion are described in Appendix A.

Spectroscopic Measurements

Gas Chromatography/Mass Spectrometry (GC/MS) and Direct Probe Mass Spectrometry (MS). GC/MS analyses were performed using a Hewlett-Packard 5985A GC/MS at 70 eV and a source temperature of 200°C. The samples were introduced into the mass spectrometer via a gas chromatograph interfaced directly to the ion source. The chromatographic column was a 30 m x 0.24 mm ID fused silica capillary column with a bonded DB-5 liquid phase (0.25 µm film thickness) (J and W Scientific, Folsom, CA). The splitless injector and GC/MS transfer line were maintained at 280°C. Helium carrier gas was maintained at a column head pressure of 16 psi. Column temperature programs for the analyses of particulate and volatile samples are listed elsewhere in this report. For methylene chloride nonextractable samples, a direct insertion probe (DIP) was used to introduce these lower volatility materials into the HP 5985 mass spectrometer in order to obtain low resolution (unit mass) spectra.

Laser Desorption Fourier-Transform Mass Spectrometry (LD FTMS). A Nicolet FTMS-2000 Fourier transform mass spectrometer equipped with a Quanta Ray Nd:YAG pulsed laser was employed in order to obtain high resolution mass spectra to confirm elemental composition. Generally, a few micrograms of each dye sample was placed on the tip of the solids probe, which was then inserted into the FTMS. The fundamental line of the laser at 1064 nm was used to generate negatively charged ions. A complete mass spectrum was obtained for each laser shot; however, due to sample ablation by laser impact, the probe was rotated after each shot for signal averaging. Accurate mass measurement (< 10 ppm mass error) could be obtained for the negatively charged molecular ions of these dyes.

Ultraviolet/Visible Spectrophotometry (UV/VIS). UV/VIS spectra were obtained on a Varian Model DMS-90 Ultraviolet-Visible Spectrophotometer (Varian Instruments, Palo Alto, CA) or on an IBM UV/Visible 9420/9430 Spectrophotometer (IBM Instruments, Inc., Danbury, CT). A known weight of each dye sample was diluted in methylene chloride to a known concentration in the range of 0.01 to 0.03 mg/mL. Spectra of these methylene chloride solutions in 1-cm quartz cells were automatically corrected for any background and cell differences during scanning by the instrument. The UV/VIS spectra of the four smoke mixes are given in Appendix C.

Nuclear Magnetic Resonance Spectroscopy (NMR). NMR spectra were obtained using a JEOL FX90 multinuclear Fourier Transform NMR spectrometer. Proton spectra were recorded at 89.56 MHz for several dye standards. In many instances, the resulting spectra contained a number of overlapping

peaks, which made interpretation very difficult; thus, only carbon-13 (^{13}C) spectra (22.5 MHz) were employed to verify compound structure. Samples were dissolved in either deuterated chloroform or d_6 -dimethyl sulfoxide at a concentration of 30 to 50 mg/mL. Approximately 1% tetramethylsilane (TMS) was added as the internal chemical shift reference. Spectra were run with internal deuterium lock either at ambient probe temperature (28°C) or at a specified elevated temperature. Typical measurement parameters were: spectrum width, 5000 Hz; pulse width, 11.5 μsec (corresponding to 45° pulse); pulse delay 5 sec; acquisition time, 0.85 sec; and the number of accumulations, 10 to 15 K. Completely decoupled spectra (COM) were obtained by broad band noise decoupling at 54.80 KHz with a bandwidth of 1 KHz. Proton coupled spectra with nuclear Overhauser effect (NOE) were obtained with the irradiation gate closed during data acquisition time. Off-resonance spectra (OFR) were obtained by setting the irradiation frequency lower than that for the complete decoupling frequency by 0.5 KHz (ie., at 54.3 KHz).

Gas Chromatography/Fourier-Transform Infrared Spectrometry (GC/FTIR). A Hewlett-Packard 5965A GC/IRD (on loan from Hewlett-Packard for a short time in our laboratory) was used to obtain GC/FTIR spectra on some of the dye materials. GC conditions were essentially the same as described in the previously outlined gas chromatography section. The spectral acquisition parameters were: scan rate, 1.5 scans/sec at scan resolution of 4 cm^{-1} ; acquisition delay, 0.00 min; pre-peak storage, 10.0s; post-peak storage, 30.0s; and storage threshold, 0.0 response units. The temperatures of the transfer line and flow cell (100 μL) were set at 280°C.

GC/FTIR spectra of the red smoke products reported in Appendix D were obtained with a recently purchased Nicolet GC/IR system, which includes a Nicolet 20SXC FTIR spectrometer and a Hewlett-Packard Model 5890 gas chromatograph. The GC oven temperature was initially set at 80°C for 2 min, then increased to 280°C at 20°C/min. Heated zones for both the transfer line and the light pipe were set at 280°. Make-up gas (helium) was added to the transfer line at 1.2 mL/min.

Particle Size Determination

The particle size distribution of the combusted colored smoke mixes was determined by using a Mercer-Lovelace seven stage cascade impactor. Duplicate samples were collected at 3 and 30 minutes after the detonation, at a flow rate of 1 L/min, for periods of less than 10 sec. The particulates, collected on individual glass stages, were dissolved in a known volume of methylene chloride. The relative mass for each stage was determined by measuring the UV/VIS absorbance of the resulting solution at λ_{\max} of each of the colored smoke mixes. The λ_{\max} values were selected from the UV/VIS spectra (given in Appendix C) and were as follows: red at 505 nm; violet at 525 nm; yellow at 442.5 nm; and green at 650 nm. Cumulative mass percentages for each stage were calculated and plotted as log normal distributions versus log of sage cut off diameters. Aerodynamic mass median diameter was determined from these plots (12). The results of these measurements are given in Appendix B.

RESULTS AND DISCUSSION

Chemical Characterization of Dye Standards

The chemical structures and registry numbers of the five synthetic dye standards, shown in Figure 1, were obtained from Chemical Abstracts (8) and from the Colour Index (9). In order to confirm their chemical structures, the major organic components of the five dye standards were first isolated and then characterized by spectroscopic methods. The results of these studies for each of the dye standards are given below.

Solvent Red 1

This dye standard (Lot No. 30100-21) is formulated to contain α -methoxybenzenazo- β -naphthol (MBN, Compound I, Figure 1). This material found to dissolve in methylene chloride or chloroform readily, but was sparingly soluble in methanol, acetone, and acetonitrile. A single reddish orange spot was observed on the TLC plates when analyzed by three different TLC plate systems, suggesting that this standard was fairly pure. The R_f values for three TLC systems were 0.33 (silica gel plate, elution with 100% methylene chloride); 0.75 (amino-bonded plate, elution with 26/48/26 ratio of hexane/benzene/tetrahydrofuran); and 0.22 (reversed-phase C₁₈-plate, elution with 90/10 mixture of methanol/water). Chromatograms of this dye standard obtained by GC as well as by HPLC (K' = 0.94, PAC column, elution with 100% methylene chloride) also revealed the presence of a single component.

Combined GC/MS was used to establish the molecular weight and fragmentation pattern of this red dye standard. As expected, the molecular ion (m/z 278), as well as several characteristic fragment ions (at m/z = 247, 171, 143 and 128) correlate well with the chemical structure of MBN. Additional structural information was obtained by GC/FTIR; the presence of the following absorption bands corroborated the assignment of this compound as MBN: aromatic stretching at 3071 cm^{-1} ; aliphatic stretching at 2949 cm^{-1} ; azo stretching at 1623 cm^{-1} ; aromatic in-plane vibration at 1507 cm^{-1} and alkyl-aryl ether stretching at 1249 cm^{-1} .

Carbon-13 NMR was used to confirm the structure of this material as MBN. Wide band proton decoupling (COM) was used to establish the chemical shift assignments. Spectral assignments were based on the chemical shifts obtained from C-13 NMR spectra of β -naphthol and azobenzene (Sadler Standard C-13 NMR Spectra, #4601 C and #79 C). The chemical shift of each carbon was calculated and compared with the experimental values. Coupling with nuclear Overhauser effect (NOE) and off-resonance proton partial decoupling (OFR) were used to facilitate these assignments. As a result of these experiments, the chemical shifts of the observed spectral lines were found to be consistent with those expected for MBN. A proton decoupled ¹³C NMR spectrum is illustrated in Figure 2, and the corresponding chemical shifts are listed in Table 1a.

Disperse Red 11

This dye standard (Lot No. 31195-057) is formulated to contain 1,4-diamino-2-methoxyanthraquinone (DMA, Compound II, Figure 1). The solubility of this material in methylene chloride or chloroform is fairly low (about 4 mg/mL). Solubility in a more polar solvent, such as acetone or dimethylsulfoxide, is slightly higher (about 30 mg/mL). A single dark reddish purple spot was visible on two different types of developed TLC plates. The R_f values on the two TLC systems were 0.67 (silica gel plate, elution with 12% acetonitrile in methylene chloride) and 0.44 (amino-bonded plates, elution with 100% methylene chloride). GC and HPLC (K' = 10.2, PAC column, elution with 100% methylene chloride) chromatograms of this dye standard also revealed the presence of a single component.

Spectra of this dye standard obtained with GC/MS revealed a molecular ion at m/z 268, as well as fragment ions at m/z 253, 225, 134 and 115, which correlate well with the chemical structure of DMA. Several absorption bands in the GC/FTIR spectrum of this dye standard further 3504 cm^{-1} ; aromatic stretching at 3077 cm^{-1} ; aliphatic stretching at 2949 cm^{-1} ; conjugated carbonyl stretching at 1640 cm^{-1} ; and alkyl-aryl ether stretching at 1269 cm^{-1} .

The chemical structure of this compound in the Disperse Red 11 dye standard was further confirmed by ^{13}C NMR. Chemical shift assignments of the observed lines were found to be in good agreement with those expected for DMA. A proton decoupled ^{13}C NMR spectrum for this compound and the chemical shift assignments are presented in Figure 3 and Table 1b, respectively. Due to the limited solubility of this compound in CDCl_3 , the spectrum was run in $d_6\text{-DMSO}$.

Disperse Blue 3

This dye standard (Lot No. 50038-001 is formulated to contain 1-(2-hydroxyethylamino)-4-(methylamino)anthraquinone (HEMA, compound III, Figure 1). When first analyzed by TLC, this dye standard appeared to be much more complex than the other four dye standards. On the TLC plates, three intense blue spots, two faint pink spots, and two faint blue spots were clearly visible. The R_f values for the three blue intense spots were 0.15, 0.58 and 0.94 (amino-bonded plate, elution with 50% acetonitrile in methylene chloride) and 0.00, 0.36, and 0.88 (silica gel plate, elution with 12% acetonitrile in methylene chloride).

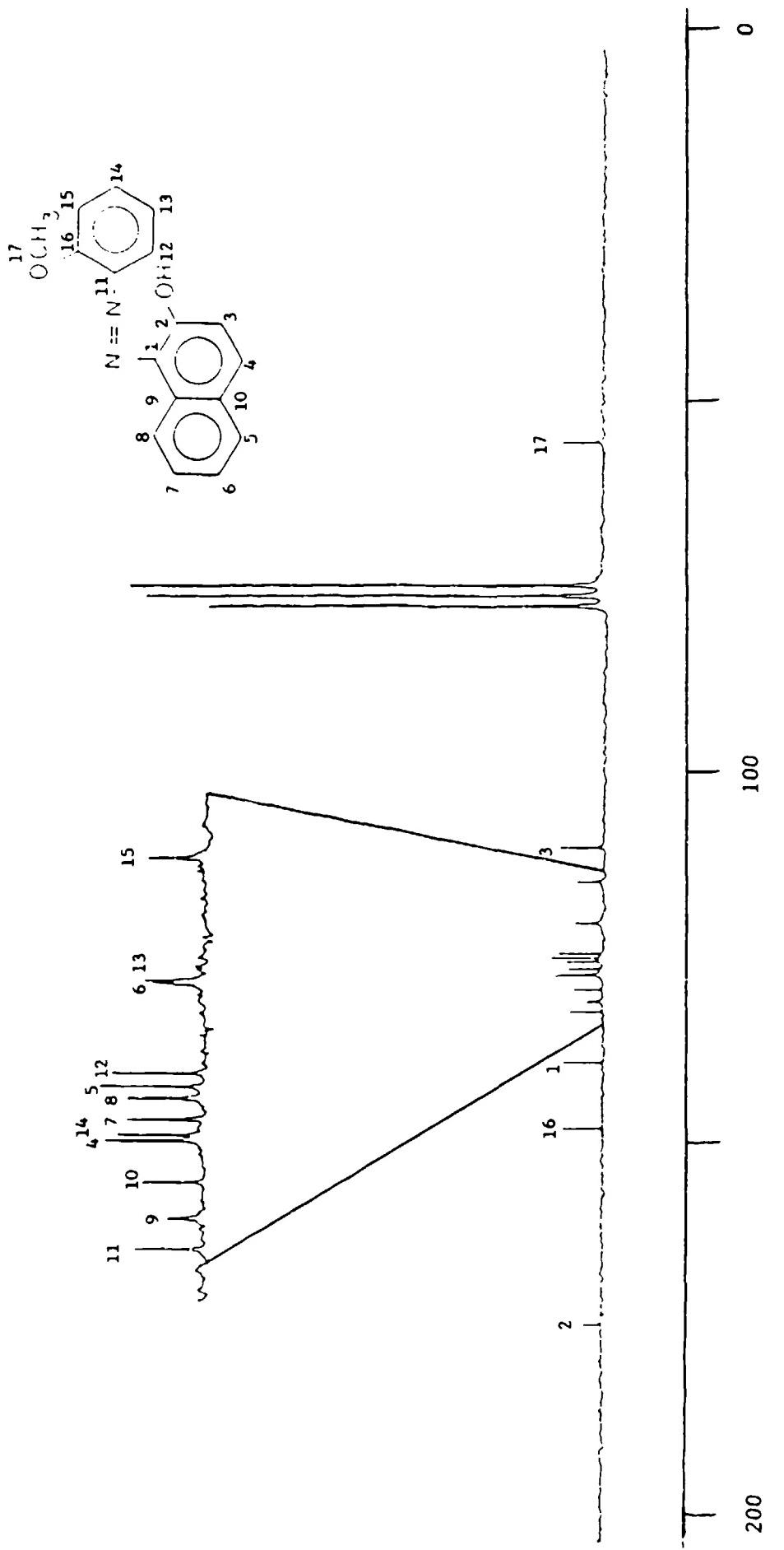


Figure 2. $C-13$ NMR Spectrum of Dye Standard Solvent Red 1 (MBN)
(See Table 1a for chemical shift assignments.)

Table 1a. ^{13}C Chemical Shifts of Solvent Red 1 (MBN)^a

Carbon No.	δ^b
1	140.8
2	176.7
3	111.3
4	128.9
5	126.4
6	121.7
7	127.9
8	126.9
9	132.4
10	130.8
11	133.8
12	125.6
13	121.6
14	128.6
15	116.0
16	149.8
17	56.0

^aSee Figure 2 for chemical structure and ^{13}C spectrum.

^bDeshielded from TMS; δ (CDCl_3) = 77.04 ppm.

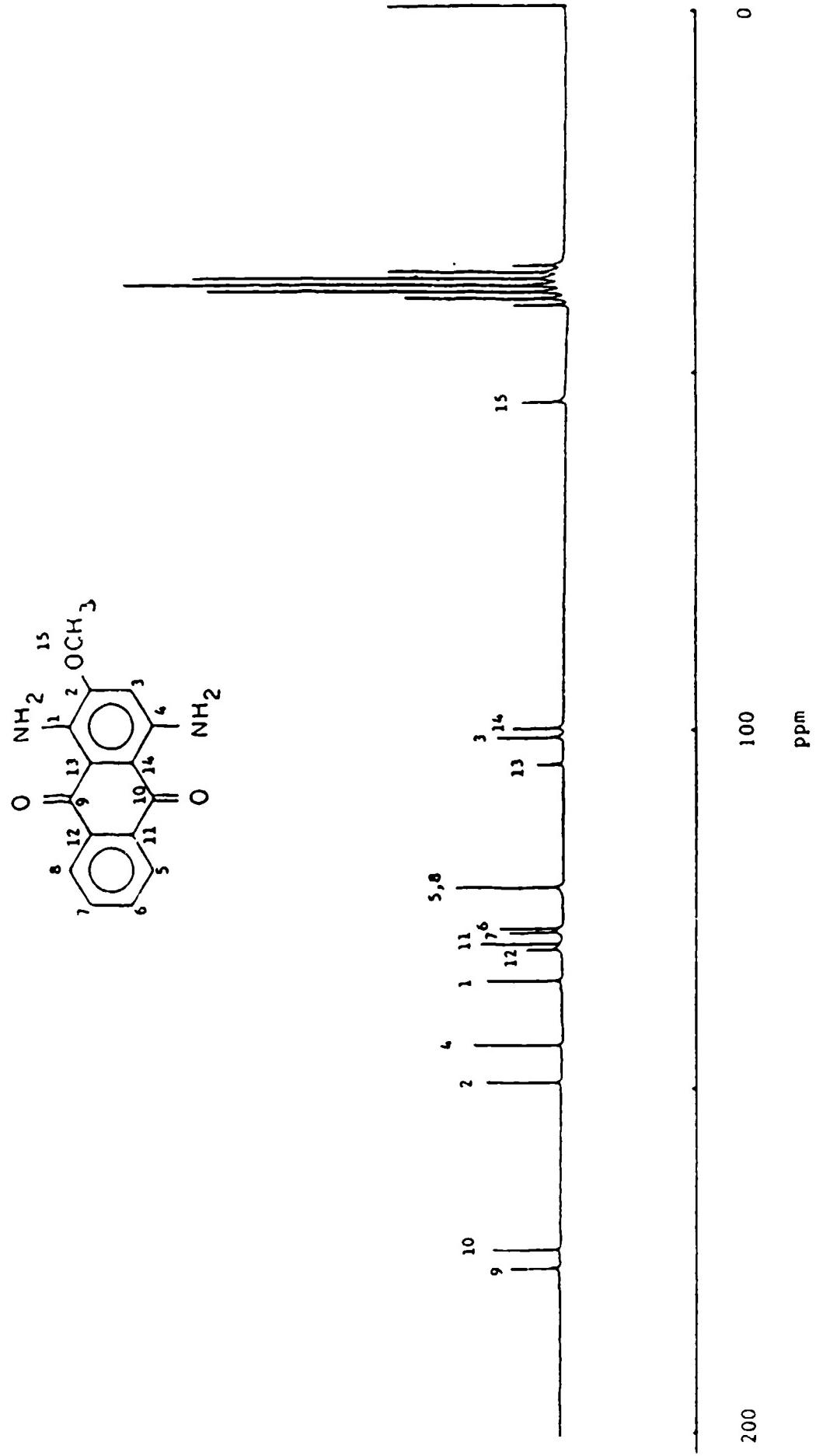


Figure 3. Carbon-13 NMR Spectrum of Dye Standard Disperse Red 11 (DMA)
(See Table 1b for chemical shift assignments.)

Table 1b. ^{13}C Chemical Shifts of Disperse Red 11 (DMA)^a

Carbon No.	δ^b
1	139.2
2	154.1
3	103.9
4	148.7
5	125.6
6	131.6
7	132.3
8	125.6
9	181.6
10	178.8
11	133.9
12	134.7
13	107.8
14	102.6
15	56.0

^aSee Figure 3 for chemical structure and ^{13}C spectrum.

^bDeshielded from TMS; δ (d_6 -DMSO) = 39.71 ppm.

Subsequent analysis by HPLC (PAC column, 100% methylene chloride elution) indicated that the blue dye standard contains at least three major and four minor components. Using GC, only two major and one minor components were visible; however, one of the major components exhibited a broad, tailing peak, suggesting that this component is fairly polar. It is most likely that the additional four components (one major and three minor) which were observed with HPLC were too polar to be eluted by GC. Soxhlet extraction of this Disperse Blue 3 dye standard with methylene chloride yielded a significant amount of residue (14.4%), which was found to be soluble in acetone or DMSO (see compound C below).

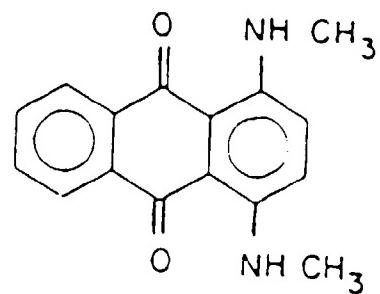
To identify the three major components, sufficient quantities of these three materials (labelled as A, B, and C) were collected from HPLC separations (PAC column, elution with 30% acetonitrile in methylene chloride) for preliminary mass spectral analyses (including GC/MS, direct probe MS and/or LD FTMS). Because the loading capacity of a semipreparative HPLC column is quite limited (less than 10 mg), a supplementary separation procedure by gravity column chromatography was devised. A 4 cm ID, 40 cm long gravity column was packed with approximately 400 g of basic alumina (activity I, 100-200 mesh) and was found to be adequate to separate 2 to 3 grams of the Disperse Blue 3 dye standard and yield approximately 100 mg of material required for ^{13}C NMR measurements. Sequential elution of this column with methylene chloride and 50% methylene chloride in acetonitrile yielded one fraction of relatively pure "Component A" and another fraction which contained "Component B" at about 90% purity (estimated by GC). Both Components A and B were purified by HPLC prior to ^{13}C NMR studies.

"Component C" was too polar to be eluted from the preparative alumina column. The methylene chloride nonextractable residue (described above) was found to contain more than 90% of "Component C". Therefore, this component was generated in 30-50 mg quantities by HPLC separation of this residue.

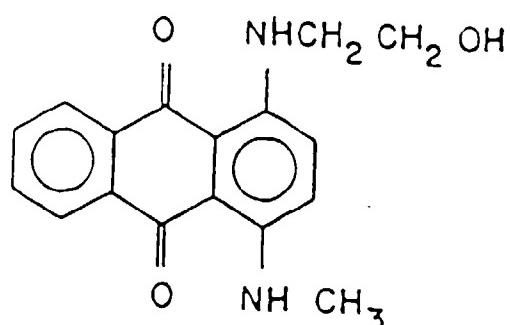
GC/MS analysis of "Component A", which represents 22 + 0.6%* of the original dye, suggested that this compound has the same molecular ion (m/z 266) and fragment ions (m/z 249, 234, 220, 165, and 152) as 1,4-bis(methylamino)anthraquinone, which is commonly called Disperse Blue 14 (CAS 2475-44-7; CI 61500, see Figure 4). Consequently, a standard of Disperse Blue 14 was purchased, and was analyzed along with "Component A" from the Disperse Blue 3 dye standard by GC, TLC, HPLC and ^{13}C NMR. The two compounds were found to be virtually identical. This compound is closely related in structure to HEMA and is most likely a byproduct of the synthesis of HEMA in the production of Disperse Blue 3 (see discussion below for "Component C"). A proton decoupled ^{13}C NMR spectrum of this compound is given in Figure 5 with spectral assignments listed in Table 1c.

*Weight percentages of the three major components were determined by HPLC and are the result of four determinations with standard derivatives ranging from 0.6 to 6.

Component A



Component B



Component C

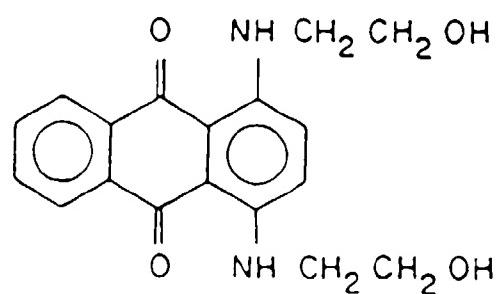


Figure 4. Chemical Structures of Major Components
in Dye Standard Disperse Blue 3

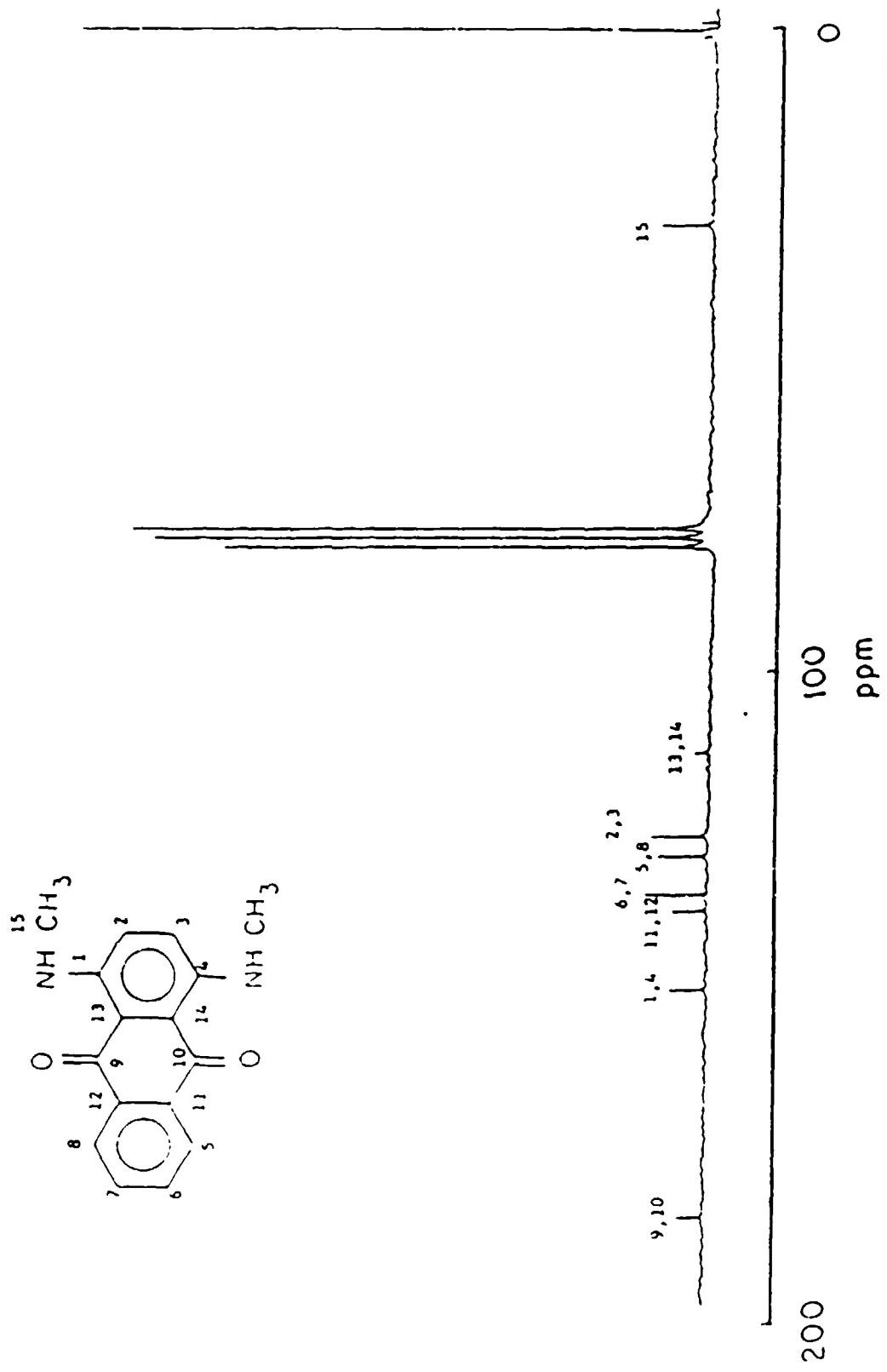


Figure 5. Carbon- 13 NMR Spectrum of 1,4-bis(methylamino)anthraquinone in Dye Standard Disperse Blue 7
(See Table 1c for chemical shift assignments.)

Table 1c. ^{13}C Chemical Shifts of 1,4-bis(methylamino)anthraquinone^a

Carbon No.	δ^b
1	146.9
2	123.0
3	123.0
4	146.9
5	126.1
6	132.0
7	132.0
8	126.1
9	183.5
10	183.5
11	134.6
12	134.6
13	110.1
14	110.1
15	29.5

^a1,4-bis(methylamino)anthraquinone, see Figure 5.

^bDeshielded from TMS; δ (CDCl_3) = 77.04 ppm.

"Component B", present at $51 \pm 3\%$ of the original Disperse Blue 3 dye standard (determined by HPLC) was analyzed first by GC/MS. Based on the molecular ion (m/z 296) and fragment ions at m/z 265, 248, 220, and 152, this component was tentatively identified as HEMA [1-(2-hydroxyethylamino)-4-(methylamino)anthraquinone, Compound II, Figure 4], which is supposed to be the sole component of Disperse Blue 3. In order to confirm this structural assignment, two additional measurements were carried out. Using negative ion laser desorption FTMS, the exact elemental formula of this component was established as $C_{17}H_{16}N_2O_3$. Carbon-13 NMR measurements in three different modes, including complete proton decoupling (COM), off-resonance decoupling (OFR), and nondecoupling with nuclear Overhauser effect (NOE), were performed on this component. The spectral assignments for the observed spectra were made based on the values of chemical shifts, multiplicity patterns due to carbon-proton spin-spin coupling, and one- and three-bond coupling constants. Results indicated that these assignments were consistent with the structure of HEMA. The proton decoupled ^{13}C NMR spectrum of this compound is given in Figure 6, with the spectral assignments listed in Table 1d.

As indicated by chromatographic analyses, "Component C" (present at $34 \pm 6\%$ as determined by HPLC) was found to be much more polar than the other two compounds, and was not amenable to GC/MS analysis. Therefore, direct insertion probe MS and negative ion laser desorption FTMS were employed to characterize this compound. Since HEMA ("Component B") is synthesized by condensation of methylamine and ethanolamine with quinizarin and leuco-quinizarin in oxidation medium (7), one possible byproduct from this reaction is 1,4-bis(2-hydroxyethylamino)anthraquinone (see Figure 4). Using low resolution direct probe MS, a molecular ion at m/z 326 and fragment ions at m/z 295, 264, 252, 247, and 236 were observed, which correlates well with this proposed structure. This assignment was also supported by the exact chemical formula ($C_{18}H_{18}N_2O_4$) as determined by high resolution LD FTMS measurement. Furthermore, chemical shift assignments of the observed ^{13}C NMR spectra were found to be in good agreement with those of the proposed structure. Thus, "Component C" was unambiguously identified as 1,4-bis(2-hydroxyethylamino)anthraquinone and a proton decoupled ^{13}C NMR spectrum is given in Figure 7, with chemical shift assignments listed in Table 1e. Since Disperse Blue 3 was used at a fairly low concentration (4.4%) in the smoke grenade formulation (Table 2), no attempt was made to characterize the minor components present in this dye standard.

Solvent Green 3

Solvent Green 3 (no lot number designated) is formulated to contain 1,4-di-p-toluidinoanthraquinone (PTA, Compound IV, Figure 1). The purity of this dye standard was checked using three different TLC systems. In each case, a single greenish blue spot was observed on the plates, with the following R_f values: 0.60 (C_{18} -reverse phase plate, elution with acetonitrile); 0.92 (amino-bonded plate, elution with methylene

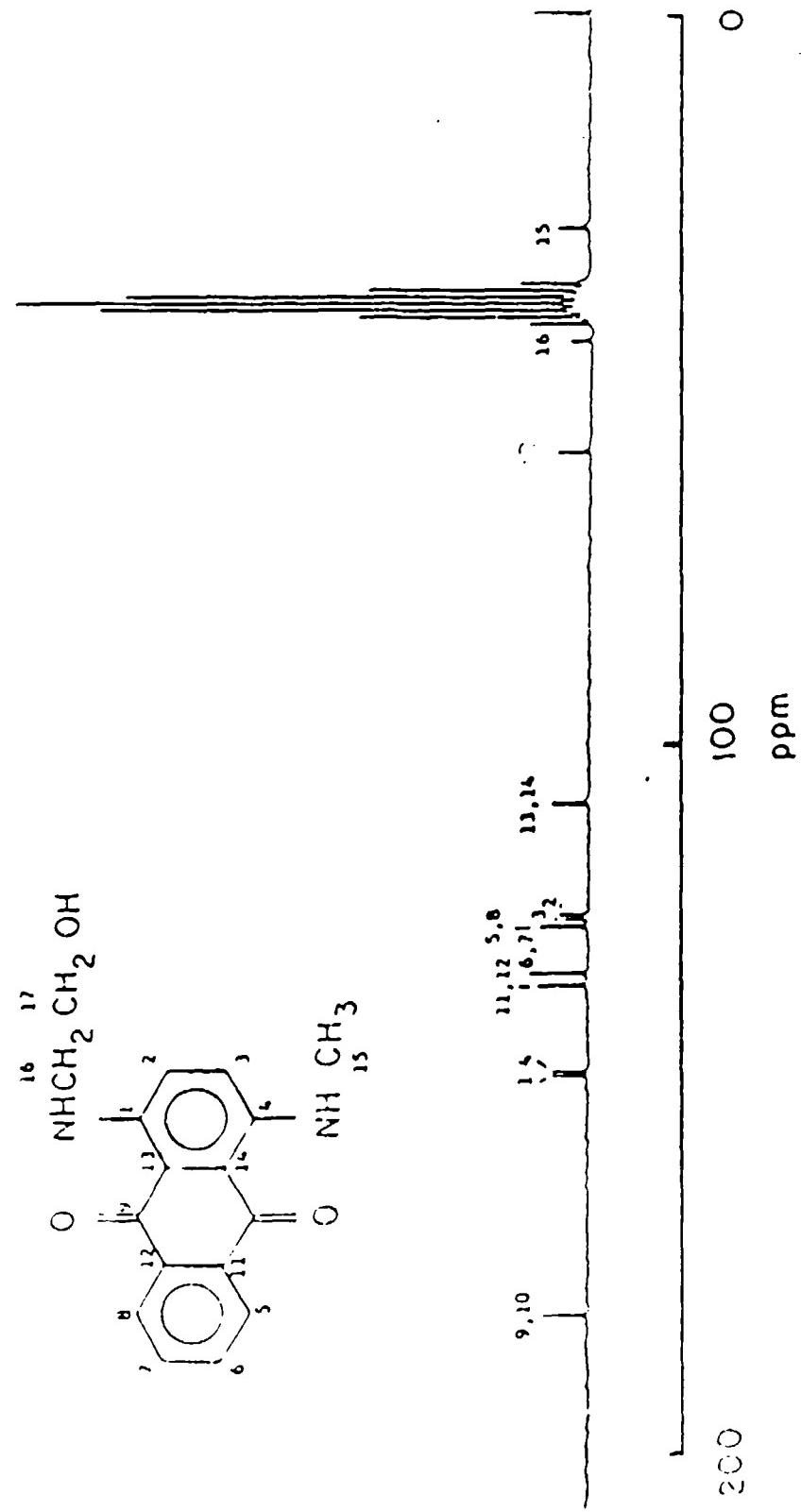


Figure 6. Carbon-13 NMR Spectrum of HEMA in Dye Standard Disperse Blue 3
(See Table 1d for chemical shift assignments.)

Table 1d. ^{13}C Chemical Shifts of Disperse Blue 3 (HEMA)*

Carbon No.	δ^b
1	146.0
2	123.8
3	124.6
4	146.6
5	125.5
6	132.0
7	132.0
8	125.5
9	180.5
10	180.5
11	133.8
12	133.8
13	108.4
14	108.4
15	29.1
16	44.7
17	59.9

*HEMA, see Figure 6.

^bDeshielded from TMS; δ (d_6 -DMSO) = 39.72 ppm.

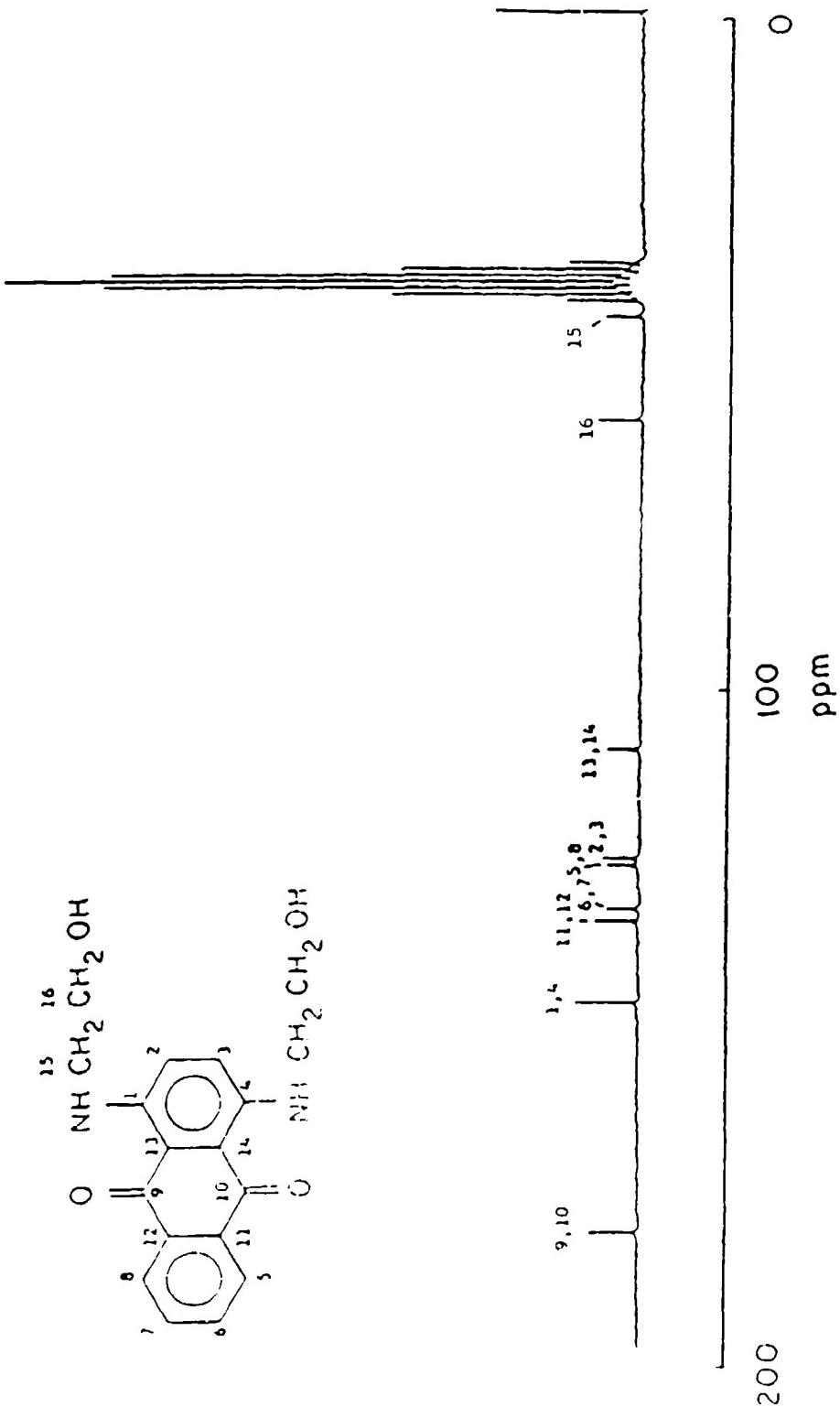
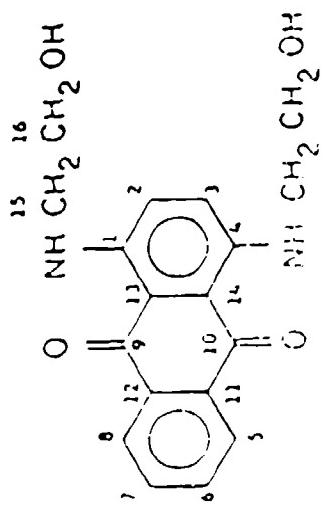


Figure 7. Carbon-13 NMR Spectrum of 1,4-bis(2-hydroxyethylamino)anthraquinone in Dye Standard Disperse Blue 3 (See Table Ie for chemical shift assignments.)

Table 1e. ^{13}C Chemical Shifts of
1,4-bis(2-hydroxyethylamino)anthraquinone^a

Carbon No.	δ^b
1	146.1
2	124.6
3	124.6
4	146.1
5	125.5
6	132.1
7	132.1
8	125.5
9	180.5
10	180.5
11	133.9
12	133.9
13	108.4
14	108.4
15	44.6
16	59.9

^a1,4-bis(2-hydroxyethylamino)anthraquinone, see Figure 7.

^bDeshielded from TMS; δ (d_6 -DMSO) = 39.72 ppm.

chloride); and 0.65 (silica gel plate, elution with methylene chloride). Subsequent analysis of this dye standard by GC and HPLC suggested, however, the presence of a trace impurity. Using GC/MS, the identity of both major and minor components were tentatively established as PTA (m/z = 418, 419, 209, 91, 77) and 1-p-toluidino-4-hydroxyanthraquinone (m/z = 329, 330, 139, 106, 77), respectively. The chemical structure of the major component was confirmed as being PTA by comparing its ^{13}C NMR spectrum with a published spectrum (2). A proton decoupled ^{13}C NMR spectrum of this material is presented in Figure 8, and chemical shift assignments are listed in Table 1f.

Solvent Yellow 33

The Solvent Yellow 33 dye standard (Lot No. 13030-006) is formulated to contain 2-(2'-quinolinyl)-1,3-indandione (QID, Compound V, Figure 1). This dye standard was found to dissolve in methylene chloride or chloroform readily, but was sparingly soluble in methanol, acetone, acetonitrile or DMSO. The purity of this dye standard was examined by three different TLC systems. A single intense yellow spot was detected on all three types of plates, with R_f values of 0.10 (silica gel plate, elution with methylene chloride); 0.72 (amino-bonded plate, elution with methylene chloride) and 0.36 (C_{18} reversed-phase plate, elution with 90% methanol in water). Using GC and HPLC ($K' = 3.56$, PAC column, elution with methylene chloride), this standard appeared to be nearly pure (>99%).

Using GC/MS, a molecular ion at m/z 273 and fragment ions at m/z 216, 204, 189 and 137 were observed, which correlates well with the reported mass spectrum of QID (Compound V, Figure 1) (10,11). Additional structural information was obtained by GC/FTIR, and the presence of the following absorption bands further substantiated the identification of this dye standard as QID: conjugated carbonyl stretching at 1637 cm^{-1} ; aromatic stretching at 3050 cm^{-1} ; and aromatic in-plane vibration at 1543 cm^{-1} .

While carrying out structural confirmation on this dye standard, a discrepancy in ^{13}C NMR spectral assignments was found in the literature (10,11). In these published reports, the chemical shift assignment was based on the assumption that the indanedione moiety (Structure II, Figure 9) is symmetrical when dissolved in d_6 -DMSO at 80°C , i.e., both quinoline and indanedione moieties undergo free rotation about the C_2-C_{10} bond (Figure 10). Consequently, in these published reports four spectral lines were assigned to the following pairs of carbons: $\text{C}_1 = \text{C}_3 = 190.3$; $\text{C}_4 = \text{C}_7 = 119.9$; $\text{C}_5 = \text{C}_6 = 132.3$ and $\text{C}_8 = \text{C}_9 = 138.9$ (Table 1b). These assignments were very different from the ^{13}C NMR spectrum (Figure 11) obtained in our laboratory when the spectra were run in CDCl_3 at 28°C . As noted in Table 1g, the spectral lines for these four pairs of carbons (listed above) were well resolved and certainly not degenerate, as indicated in the published spectrum. In order to verify that QID was indeed the only compound present in this dye standard, three additional

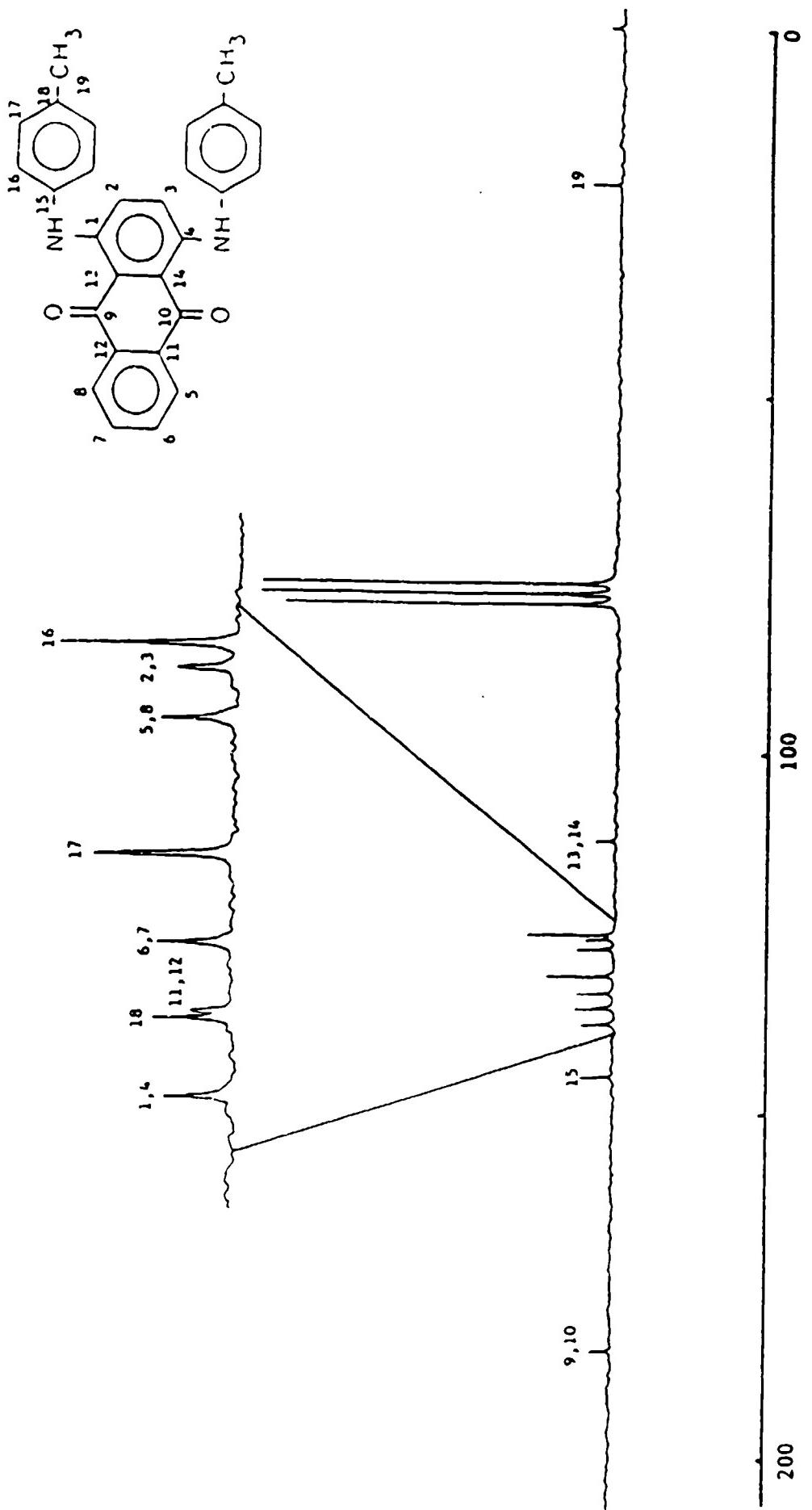


Figure 8. ^{13}C NMR Spectrum of Dye Standard Solvent Green 3 (PTA)
(See Table I for chemical shift assignments.)

Table 1f. ^{13}C Chemical Shifts of Solvent Green 3 (PTA)^a

Carbon No.	δ^b
1	136.8
2	125.0
3	125.0
4	136.8
5	126.3
6	132.6
7	132.6
8	126.3
9	183.2
10	183.2
11	134.4
12	134.4
13	111.1
14	111.1
15	144.3
16	124.2
17	130.1
18	134.6
19	21.0

^aSee Figure 8 for chemical structure and ^{13}C spectrum.^bDeshielded from TMS; δ (CDCl_3) = 77.04 ppm.

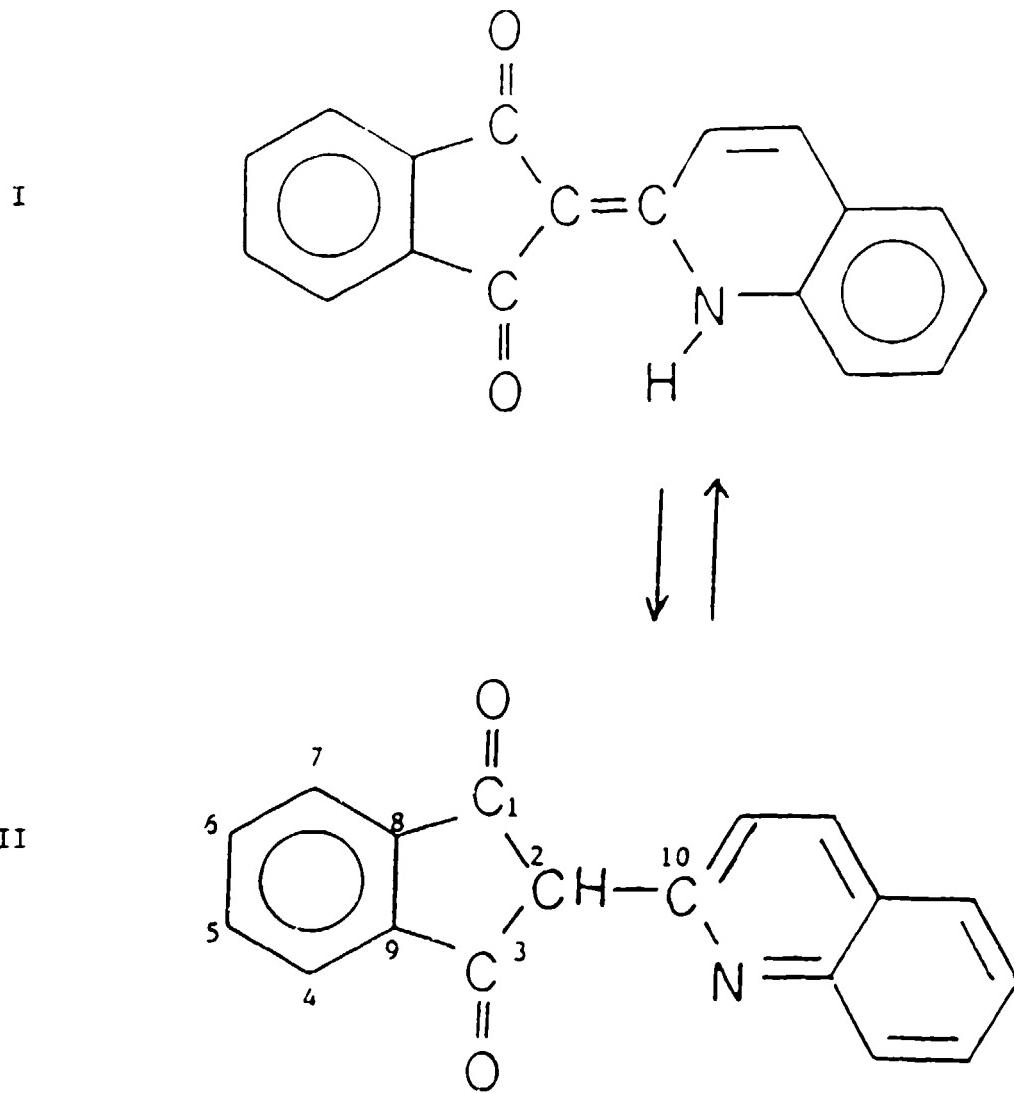


Figure 9. Tautomeric Structures of Dye Standard Solvent Yellow 33 (QID)

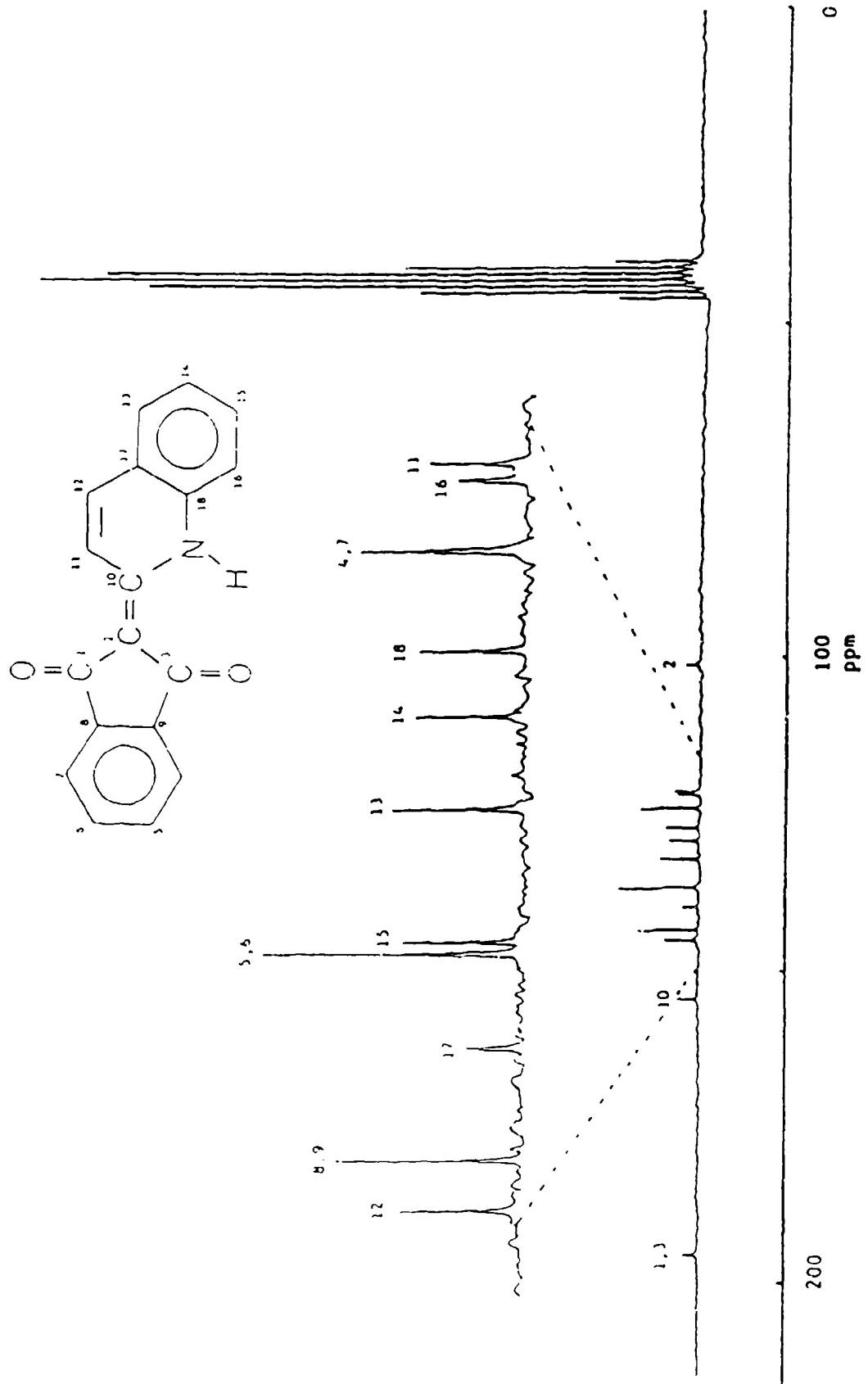


Figure 10. Carbon-13 NMR Spectrum of Dye Standard Solvent Yellow 33 (QID) in $\text{d}_6\text{-DMSO}$ at 80°C
(See Table 1g for chemical shift assignments.)

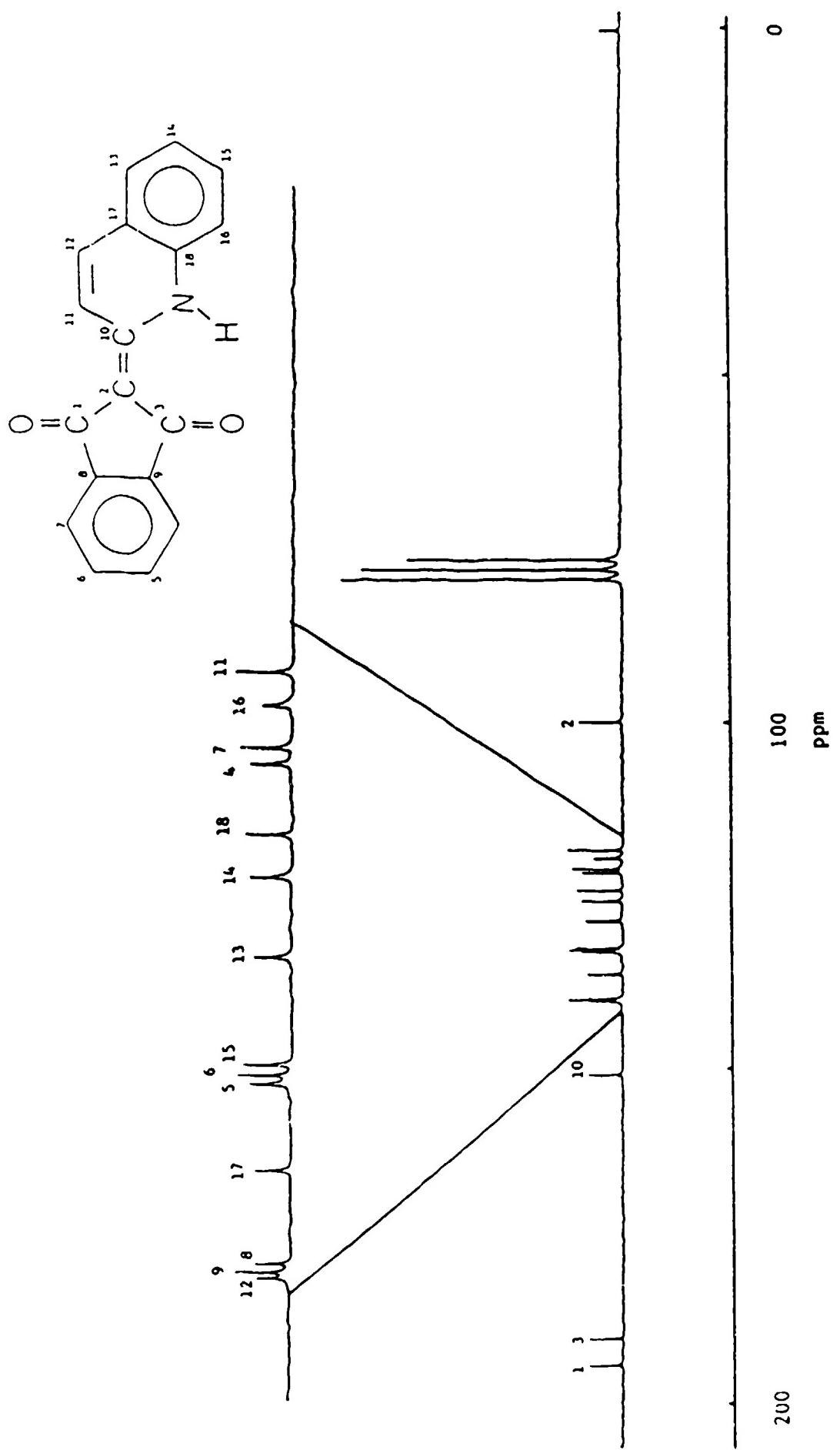


Figure 11. Carbon-13 NMR Spectrum of Dye Standard Solvent Yellow 33 (QID) in CDCl_3
(See Table 1g for chemical shift assignments.)

experiments were performed. First, this standard was re-examined using several chromatographic systems (GC, TLC, HPLC) to establish the fact that this standard contains only one component. Secondly, this dye standard was subjected to high resolution LD FTMS analysis to scrutinize the exact elemental formula. Results indicated that this standard possesses the correct elemental formula ($C_{18}H_{14}N_1O_2$) for either isomer of QID (Structures I or II, Figure 9). Thirdly, ^{13}C NMR measurements of this dye standard were obtained using the same experimental conditions as stated in the literature (d_6 -DMSO, at $80^\circ C$). Under these conditions, the resulting spectra (Figure 10) and the spectral data reported in the literature were virtually identical (Table 1g). Based on these observations, it is reasonable to conclude that the differences in chemical shift values can be attributed to the degree of imine-enamine tautomerism (Figure 9) involving the bond (C_2-C_{10}) connecting the quinoline and indanedione moieties. This tautomerism appears to be temperature as well as solvent dependent.

Table 1g. ^{13}C Chemical Shifts of Dye Standard Solvent Yellow 33 (QID)^a

Carbon No.	$CDCl_3$	d_6 -DMSO ^c	Literature ^d
1	194.4	190.4	190.3
2	99.1	97.9	97.8
3	190.3	190.4	190.3
4	121.1	120.1	119.9
5	132.8	132.5	132.3
6	132.5	132.5	132.3
7	120.5	120.1	119.9
8	139.5	139.0	138.9
9	139.8	139.0	138.9
10	150.8	149.8	149.7
11	117.8	117.4	117.4
12	140.0	140.6	140.5
13	128.2	128.0	127.9
14	125.3	125.1	125.0
15	132.1	132.1	132.0
16	119.0	118.0	117.9
17	136.0	135.5	135.4
18	123.9	123.1	123.0

^aDeshielded from TMS; $\delta(CDCl_3) = 77.04$ ppm; $\delta(d_6\text{-DMSO}) = 39.72$ ppm.

^bSee Figure 11 for chemical structure and ^{13}C spectrum.

^cSee Figure 10 for chemical structure and ^{13}C spectrum.

^dReferences 10 and 11.

^eAssignment may be interchanged.

Chemical Characterization of Colored Smoke Mixes Before and After Combustion

Red Smoke Mix

Uncombusted Red Smoke. The red smoke grenade is formulated to contain Solvent Red 1 (MBN) and Disperse Red 11 (DMA) at a ratio of 5 to 1, as well as other materials, as shown in Table 2. These two smoke mixes were obtained from Pine Bluff Arsenal and characterized using procedures similar to those used for the analysis of the dye standards described above. Both of these materials were found to contain virtually the same components as the previously analyzed dye standards. Soxhlet extraction of these smoke mixes resulted in the isolation of 3.1% of residue in the Solvent Red 1 and 6.0% in Disperse Red 11. Direct insertion probe mass spectrometry was used in an attempt to identify the constituents in these two residues. Even at a probe temperature of 280°C, the major portion of these residues remained as nonvolatile solids. The volatile components exhibited several characteristic fragmentations suggesting the presence of phthalate esters and hydrocarbons.

Because the red smoke grenades were formulated by mixing the two smoke mixes, a synthetic red smoke mix was prepared by mixing Solvent Red 1 with Disperse Red 11 at the same ratio (5 to 1) as present in the grenade formulation. This synthetic red smoke mix test material was used to evaluate possible isolation and spectroscopic methods for the analysis of the combusted smoke mixes and was also analyzed in parallel with the combusted smoke mixes to compare changes in composition upon combustion.

Combusted Red Smoke Particulates. The first combustion experiment with red grenades was conducted on August 5, 1987. As described in the experimental section, airborne particulates from the combusted colored smoke grenades were collected either in glass trays (fallout) or into a high volume sampler (HVS). The particulate sample collected from the combusted red grenade can best be described as dark reddish black, amorphous substance, which adhered to the wall of the tent and the collection devices as an oily thin film. This material was quite different than that obtained with previous grenades (1,3), which was light, fluffy, and intensely colored. A total of 2.7 grams of this substance was recovered from six glass trays, and 2.2 grams from the HVS.

Because of the seemingly abnormal nature of the combustion of the first red grenade, this combustion experiment was repeated on September 9, 1987. During this combustion experiment, the two window flaps inside the combustion chamber were kept open and clear plastic sheets were taped over the openings for observation. Three consecutive combustions were conducted at about one-hour intervals, due to reasons outlined below. Because a very limited quantity of fallout particulates were generated

in each test, the same combustion chamber was used for all three combustion experiments of the red grenades. For the collection of volatile samples and airborne particulate matter, fresh XAD and Tenax tubes and cellulose thimbles were used for each combustion test.

Table 2. Composition of Colored Smoke Grenades

Colored Smoke Mixes	Constituent	Lot Number	Weight %
M18 Red	Solvent Red 1	30100-23	34.2
	Disperse Red 11	0119J-001	6.8
	Sugar	6795	17.7
	Magnesium Carbonate	106	9.6
	Terephthalic Acid	HUE 5177	14.0
	Potassium Chlorate	S30-005-001	17.7
	Stearic Acid	-	50
M18 Violet	Disperse Red 11	01195-001	38.0
	Disperse Blue 3	50038-001	4.4
	Sugar	6795	22.26
	Magnesium Carbonate	106	13.84
	Potassium Chlorate	830-005-001	21.5
M18 Green	Green Smoke Mix VII*	RJC-83K-003	42.0
	Sugar	6795	17.5
	Magnesium Carbonate	106	15.5
	Potassium Chlorate	830-005-001	25.0
M18 Yellow	Solvent Yellow 33	RJC-83C-007	42.0
	Sugar	6795	16.4
	Magnesium Carbonate	106	17.5
	Potassium Chlorate	830-005-001	24.1

*Green Smoke VII contains 70% Solvent Green 3 and 30% Solvent Yellow 33

In all three combustion experiments with the red grenades, a very similar burning pattern was observed. At the instant of detonation, a bright flame was clearly visible through the window openings, with a plume of red smoke pushing downward from the bottom of the grenade. Within a few seconds, the red smoke appeared to catch flame, and the flames spread over the gravel surface in the galvanized tub over which the grenade was suspended. Simultaneously, light greyish smoke was generated and filled the combustion chamber. The flaming lasted about two minutes, which was considerably longer than had been observed in previous tests (1,5) with M18 smoke grenades. Sample collection was stopped at approximately 45 minutes. Particulate collection devices, such as the Cambridge filter pads and HVS thimble, were filled with a charcoal-black powder. However, only a trace amount of black fallout particulates were recovered from the glass trays.

On December 16, 1987, the detonation experiment on a second shipment of red smoke grenades (received November 16, 1987) was conducted. A total of five grenades were detonated consecutively in a single sampling chamber. Detonation of the first grenade generated a small amount of red smoke. However, the particulate matter collected in the HVS, as well as in the glass trays, was a dark reddish-black, amorphous substance, similar to the material collected from the first detonation experiment of a red smoke grenade conducted on August 5, 1987. The remaining four red smoke grenades underwent complete combustion at the instant of detonation, characterized by considerable flaming, followed by generation of large quantities of dark greyish smoke. The combustion pattern was very similar to those observed during the earlier three detonation experiments conducted on September 9, 1987.

From a total of nine red smoke grenades which have been detonated, it was believed that suitable samples for the chemical characterization of the red smoke grenade were not obtained. As noted above, the material collected from the combustion of the red smoke grenade was not thought to be characteristic of a "normal" smoke. Therefore, the results presented in this section are obtained from the initial burn conducted on August 5, 1987. As mentioned above, these experiments were repeated several times, but in each case the combustion was questionable; therefore, the data given below are offered only for informational purposes. It is obvious that these experiments need to be repeated to obtain more reliable data. [NOTE: A third shipment of red grenades was received on April 20, 1988, and represented a new formulation. One of the grenades was detonated and behaved normally, producing large quantities of bright red smoke. The chemical characterization of this smoke is presented in Appendix D. It was determined that the composition of the red particulate did not vary significantly qualitatively from the "abnormal" grenades, but quantitative differences were observed.]

Red smoke particulates recovered from the high volume sampler (HVS) and from the glass trays (fallout) were first subjected to Soxhlet extraction with methylene chloride for 6 hours. The two extracts were then analyzed by GC and GC/MS to characterize the major components in these two samples. A list of compounds showing tentative identification, is presented in Table 3. Two of these components were identified more confidently as the two unaltered original dyes MBN and DMA by comparing their GC retention times and mass spectra with those obtained from the dye standards. Several others, as noted on Table 3, were more confidently assigned based on GC/FTIR and/or FTMS data obtained from characterization of the products from the third lot of grenades (See Appendix D). The weight distributions of the components present in the particulates were determined by GC, using anthracene as an internal standard. For comparison, the same procedure was also carried out with the synthetic red smoke mix, which was described above.

As indicated in Table 3, the weight percent for unaltered MBN and DMA in both fallout and HVS particulate samples decreased when compared to

Table 3. Composition of Red Smoke Grenade Particulates and Synthetic Red Smoke Mix

Methylene Chloride Extractable	Weight % ^a				Relative Composition ^c	
	Smoke Mix	Combustion Particulates Fallout	HVS	Smoke Mix	Combusted Particulates Fallout	HVS
α-methoxybenzenazo-β-naphthol (MBN)	89	35	26	100	100	100
1,4-diamino-2-methoxyanthraquinone (DRA)	15	7	5	17	20	18
α,β-diaminobenzoquinones	<0.1	ND	ND	<1	-	-
2-Methoxyaniline ^d	ND	4	5	-	11	18
β-acetylmethoxyaniline	ND	<0.1	ND	-	0.3	-
β-formylmethoxyaniline	ND	ND	<0.1	-	-	0.4
2-Naphthol ^d	ND	1	0.3	-	3	1
Naphtho-(1,2-d)oxazole^d	ND	4	4	-	11	14
C₁-naphtho-(1,2-d)oxazole^d	ND	0.5	0.2	-	1	0.7
Anisomethyl	ND	0.1	ND	-	0.2	-
Methoxyphenylnaphthal^d	ND	2	1	-	6	6
Total Extractable Material (wt%) ^b	98.4	96.3	95.5			
Residue	1.6	3.7	4.5			

^aDetermined by GC, wt% of the extractable material^bDetermined gravimetrically, wt% of the original material^cCalculated on the basis of the major component being set arbitrarily at 100%^dAssignments were more confidently assigned using GC/FID and/or FTMS (see Appendix D)^eHold type - tentative assignment; others confirmed by chromatography

ND = not detected

the uncombusted smoke mix. It was also noted that significant amounts of 2-methoxyaniline and 2-naphthol were found in both combusted samples. These two compounds are probably the decomposition products from the combustion of MBN, resulting from cleavage of the d azo bond. Another possible decomposition product, Naphtho-(1,2d)-oxazole, was also present at significant concentrations in the combustion samples. A trace quantity of aminonaphthol was detected in the fallout particulates but not in the HVS particulates. Overall, the composition and weight distribution for both HVS and fallout particulate samples were nearly the same.

Violet Smoke Mix

Uncombusted Violet Smoke Mix. The violet smoke grenade is formulated to contain Disperse Red 11 and Disperse Blue 3 at ratios of 8.6 to 1.0 along with other components, as shown in Table 2. The analysis of the Disperse Red 11 smoke mix, which is also a component in the red smoke grenade, was discussed above. The composition of the Disperse Blue 3 smoke mix was found to be essentially identical to the Disperse Blue 3 dye standard previously studied and discussed above. A significant amount of nonextractable material (14%) was recovered after Soxhlet extraction of this smoke mix with methylene chloride. More than half of this material (52%) was found to be soluble in acetone and was identified as 1,4-bis(2-hydroxyethylamino)anthraquinone ("Component C" from Disperse Blue 3). Direct probe mass spectrometry was used to characterize the remaining constituents of this nonextractable material. The major portion of this material remained as nonvolatile solids, although traces of phthalate esters and hydrocarbons were observed.

A synthetic violet smoke mix was made by mixing Disperse Red 11 and Disperse Blue 3 in the same ratios as in the violet smoke grenades, 8.6 to 1.0. As was done in the case of the red smoke grenade, this synthetic mix was used to develop suitable isolation and characterization methods for employment with the combusted dye material and to compare composition changes due to combustion.

Combusted Violet Smoke Particulates. Portions of the violet particulates removed from the HVS (6 g), those from the glass trays (5 g fallout), and the synthetic violet smoke mix, were extracted continuously with methylene chloride in a Soxhlet extractor for approximately 14 hours. The extracts from these three sources were first analyzed by TLC to determine their complexity. The results indicated the presence of at least five components in the two combusted particulate samples and four components in the uncombusted sample. The complexities of these samples were presumed to arise from the multiple components present in one of the original dyes, Disperse Blue 3.

The methylene chloride extractable fractions were further analyzed by GC and GC/MS to characterize the major components in the samples. A list of the compounds identified is present in Table 4. The unaltered

Table 4. Composition of Violet Smoke Grenade Particulates and Synthetic Violet Smoke Mix

Methylene Chloride Extractable	Weight %	Relative Composition ^d			
		Smoke Mix		Combusted Particulates	Smoke Mix
		Fallout	HVS	Fallout	HVS
1,4-diamino-2-methoxyanthraquinone (DMA) ^a	95	55	65	100	100
1,4-bis(methylamino)anthraquinone ^a	5	4	4	5	7
1-(2-hydroxyethylamino)-4-(methylamino)-anthraquinone (HEMA) ^a	6	4	2	6	7
1,4-bis(2-hydroxyethylamino)anthraquinone ^a	3	ND	ND	3	-
1-aminoanthraquinone ^b	ND	1	0.3	-	2
Aminosmethoxyanthraquinone ^b	ND	1	1	-	2
1,4-diamino-anthraquinone ^b	ND	2	2	-	4
1-amino-4-methylaminoanthraquinone ^b	ND	3	3	-	5
Methyl-substituted DMA ^b	ND	3	3	-	5
Dimethyl-substituted DMA ^b	ND	1	3	-	2
Total Extractable Material (wt%) ^c	96.8	96.6	99.4		
Residue	3.2	3.4	0.6		

^adetermined by HPLC, wt% of the extractable material^bdetermined by GC, wt% of the extractable material^cdetermined gravimetrically, wt% of the original material^dcalculated on the basis of the major component being set arbitrarily at 100%

bold type - tentative assignment; others confirmed by chromatography

ND = not detected

dyes, DMA, HEMA, and 1,4-bis(methylamino)anthraquinone and 1,4-bis(2-hydroxyethylamino)anthraquinone were confidently identified when their GC and HPLC retention times and mass spectra were compared with those obtained for the previously studied dye standards. Confident identification of 1-aminoanthraquinone and 1,4-diamino-anthraquinone was made by comparing their GC retention times and mass spectra with those obtained from the commercially available standards. Because several components, such as HEMN and 1,4-bis(2-hydroxyethylamino)anthraquinone (present in the Disperse Blue 3 dye standard) were too polar to be analyzed by GC, the weight percentages of all the major components (as noted in Table 4) were estimated by HPLC. The weight percentages of the remaining components were estimated from GC peak heights, assuming their response factors were the same as DMA.

As indicated in Table 4, in both combusted samples, more than 50% of DMA from Disperse Red 11 and substantial amounts of 1,4-bis(methylamino)anthraquinone and HEMA from Disperse Blue 3 remained unaltered during the combustion process. However, no unaltered 1,4-bis(2-hydroxyethylamino)anthraquinone from Disperse Blue 3 was detected in either the HVS or fallout particulates.

It should be noted that small amounts of 1-aminoanthraquinone and 1,4-diaminoanthraquinone were found in both HVS and fallout particulate samples. These two compounds are probably decomposition products from the combustion of either DMA or HEMA, since both of these dyes contain the 1,4-diaminoanthraquinone moiety. These same combustion products, 1-aminoanthraquinone and 1,4-diaminoanthraquinone, were also observed in previous studies (1,5) of combusted smoke mixes from a red smoke mix containing 1-methylaminoanthraquinone (MAA) and a violet smoke mix containing 1,4-diamino-2,3-dihydroanthraquinone (DDA), respectively. In these prior studies, both of these combustion products exhibited significant bacterial mutagenicity.

The compound tentatively identified as an aminomethoxyanthraquinone is most likely the product of DMA, as are the components which appear to be methyl- and dimethyl-substituted derivatives of DMA. The tentatively assigned compound, 1-amino-4-methylaminoanthraquinone, is most likely a decomposition product from any of the three components observed in the Disperse Blue 3 dye standard: 1,4-bis-(methylamino)anthraquinone, 1-(2-hydroxyethylamino)-4-(methylamino)anthraquinone (HEMA), and 1,4-bis(2-hydroxyethylamino)anthraquinone.

Yellow Smoke Mix

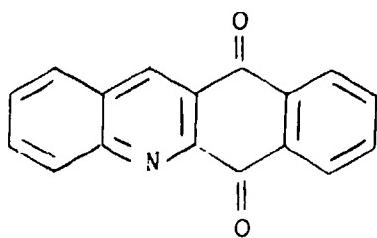
Uncombusted Yellow Smoke Mix. The yellow smoke grenade is formulated to contain only Solvent Yellow 33 (QID), as well as some other nondye materials, as shown in Table 2. The actual smoke mix used in the construction of the tested grenades was received from Pine Bluff Arsenal and analyzed in a manner similar to the Solvent Yellow 33 dye standard, described previously. The composition of the smoke mix was found to be essentially the same as the dye standard. A small amount

(3.7%) of nonextractable material remained after Soxhlet extraction of the Solvent Yellow 33 smoke mix. Direct probe mass spectrometry revealed the presence of some phthalate esters and hydrocarbon-related compounds in these nonextractable materials, although most of the material was not volatilized and thus could not be analyzed.

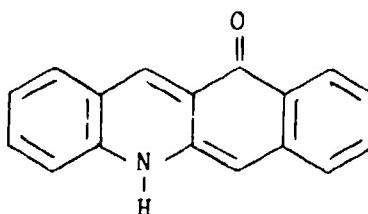
Combusted Yellow Smoke Particulates. The quantities of particulates recovered from the combusted yellow grenade were considerably less than was recovered from the combustion of green and violet grenades, i.e., 1.4 grams from glass trays (fallout) and 2.5 grams from the HVS. The material collected was a dry, fluffy, fine yellow powder, typical of a grenade combustion. The particulate samples were characterized using analytical procedures previously used to characterize the Solvent Yellow 33 dye standard. For comparison, an uncombusted sample of yellow smoke mix, which was used in the construction of the yellow smoke grenades, was also analyzed using the same procedure as the combusted particulates.

The methylene chloride extracts from these three samples (uncombusted smoke mix, fallout and HVS) were all the same dark brownish yellow color. However, a substantial amount (5 to 9.9%) of black material remained as residue from the Soxhlet extraction of the two types of combusted particulates.

Subsequent analyses of the methylene chloride extractable fractions by TLC and GC revealed the presence of one major and three or four minor components in the combusted samples, and only one component in the uncombusted smoke mix. The major component in the combusted sample was isolated by HPLC and subsequently analyzed by GC/MS and ^{13}C NMR. Results indicated that the structure of this component is consistent with that of QID, the major component of Solvent Yellow 33 (Table 5). The three minor components were tentatively identified by GC/MS as products from the combustion of Solvent Yellow 33, and 10H-2,3-benzacridine-1,4-dione (I, mw 259), 10H-2,3-benzacridine-1-one (II, mw 245) and an isomer of 2,3-benzacridine-1,4-dione (mw 259). Another component exhibited the same molecular ion and fragment ions as observed in the mass spectrum of QID, but with a different GC retention time. Therefore, this compound was identified as an isomer of QID.



I



II

Table 5. Composition of Yellow Smoke Grenade Particulates and Yellow Smoke Mix

Methylene Chloride Extractable	Weight %			Relative Composition ^d		
	<u>Smoke Mix</u>	<u>Combusted Particulates</u>	<u>Smoke Mix</u>	<u>Combusted Particulates</u>	<u>Fallout</u>	<u>HVS</u>
	<u>Fallout</u>	<u>HVS</u>				
2-(2'-quinoliny)-1,3-indandione (QID) ^a	100	71	76	100	100	100
10B·2,3-benzacridine-9-one^b	ND	3	0.5	-	4	0.7
2,3-benzacridine-1,4-dione^b	ND	0.5	>0.1	-	0.7	<0.1
Isomer of 2,3-benzoacridine-1,4-dione^b	ND	0.9	ND	-	1	ND
Isomer of QID^b	ND	0.3	<0.1	-	0.4	<0.1
Total Extractable Material (wt%) ^c	96.3	90.1	95.1			
Residue	3.7	9.9	4.9			

^a determined by HPLC, wt% of the extractable material^b determined by GC, wt% of the extractable material^c determined gravimetrically, wt% of the original material^d calculated on the basis of the major component being set arbitrarily at 100%

bold type - tentative assignment; others confirmed by chromatography

ND = not detected

The weight percent of QID in the three samples (given in Table 5) was determined by HPLC, while the weight distributions of the remaining components were estimated based on the area integration of GC peaks, assuming their response factors were the same as QID. As noted in Table 5, a large portion of the extractable material remained as unaltered QID (Solvent Yellow 33) in both the HVS and fallout particulates, while the level of detectable minor components was slightly higher in the fallout sample than in the HVS sample.

Green Smoke Mix

Uncombusted Smoke Mix. Green Smoke VII is a mixture of two of the dye mixes, Solvent Green 3 and Solvent Yellow 33. After separation of the methylene chloride extractable fraction by HPLC, the major components of this green smoke mix were found to be 68.0% 1,4-di-p-toluidino-9,10-anthraquinone (PTA, Compound IV, Fig. 1) and 25.7% of 2-(2'-quinolinyl)-1,3-indandione (QID, Compound V, Fig. 1), as shown in Table 6. A trace quantity (0.7%) of 1-p-toluidino-4-hydroxyanthraquinone (THA) was detected in this smoke mix, as well, and is most likely a synthetic intermediate of PTA. The methylene chloride nonextractable fraction was analyzed by direct probe MS, and was observed as in the other smoke mixes, the major portion remained as nonvolatile solids. The volatile components exhibited several characteristic fragmentations suggesting the presence of phthalate esters and hydrocarbons.

Combusted Green Smoke Particulates

A total of 9.1 grams of green particulates was recovered from the glass trays (fallout) and 6.0 grams from the high volume sampler (HVS). Particulates from these two sources, along with the uncombusted green smoke mix (Green Smoke Mix VII), were first subjected separately to Soxhlet extraction with methylene chloride for approximately eight hours. The three extracts were then concentrated and analyzed by GC and TLC. TLC results indicated that at least three components were common to the two sources of combusted particulate extracts (i.e., fallout and HVS). Of these compounds, two exhibited the same R_f values as PTA and QID. The gas chromatograms of the two combusted particulate extracts indicated two major components and two minor components in each. To characterize these components, these two extracts, as well as the extracts from the uncombusted Green Smoke Mix VII, were studied further by GC/MS. A list of the compounds tentatively identified is presented in Table 6.

Two major components were identified as the unaltered original dyes PTA and QID, because their GC and HPLC retention times and mass spectra were identical to those previously obtained from these dye compounds. Sufficient quantities of these two components were isolated from the particulates by a gravity LC column and subjected to ^{13}C NMR analysis, which supported these structural assignments.

Table 6. Composition of Green Smoke Grenade Particulates and Green Smoke Mix VII

Methylene Chloride Extractable	Weight %	Relative Composition ^d			
		Smoke Mix	Combusted Particulates HVS	Fallout	Combusted Particulates HVS
1,4-di-p-toluidinoanthraquinone (PTA) ^a	68	58	58	100	100
2-(2'-quinalinyl)-1,3-indandione (QID) ^a	26	27	26	38	47
1-p-toluidino-4-hydroxy-anthraquinone (THA)^b	0.7	0.8	0.3	1	0.5
1-p-toluidino-6-anthraquinone (TA)^b	ND	2	1	-	3
Isomer of QID^b	ND	0.3	0.2	-	0.5
Total Extractable Material (wt%) ^c	99.9	96.6	96.8		
Residue	0.1	3.4	3.2		

^adetermined by HPLC, wt% of the extractable material^bdetermined by GC, wt% of the extractable material.^cdetermined gravimetrically, wt% of the original material^dcalculated on the basis of the major components being set arbitrarily at 100%

bold type - tentative assignment; others confirmed by chromatography

ND = not detected

Trace quantities of a third compound (< 1%), tentatively identified as 1-p-toluidino-4-hydroxyanthraquinone (THA), was detected in both combusted samples, and was also present in the uncombusted mix, as discussed previously. Two other compounds in the combusted smoke particles were tentatively identified as 1-p-toluidinoanthraquinone (TA) and an isomer of QID. The compound TA is most likely a decomposition product from the combustion of PTA.

The weight percentages of the compounds in the combusted smoke mixes are given in Table 6. Because the GC retention time of PTA was impractically long, its weight percentage was determined instead by HPLC (PAC column, elution with methylene chloride). The weight percentage of THA and the isomer of QID were estimated from the area integration of GC peaks, assuming their response factors were the same as QID. Because TA was not completely resolved from QID by GC, its weight percentage was estimated based on the area integration of its molecular ion (m/z 313), using the selective monitoring mode during MS analysis and assuming the response factor of TA is the same as QID.

As indicated in Table 6, in samples from both the HVS and fallout, the weight distributions for PTA and QID, as well as for the minor components, were found to be almost the same. Furthermore, it was observed that a small fraction of PTA was altered during the combustion process, while QID remained relatively unchanged upon combustion of Green Smoke VII.

CONCLUSIONS

Five dye standards supplied by USABRDL were chromatographically tested to assess purity using TLC and HPLC. The major components were separated by HPLC or gravity LC and then characterized spectroscopically using mass spectrometry (GC/MS, direct probe MS, and/or laser desorption FTMS), ^{13}C nuclear magnetic resonance, and Fourier transform infrared. Results indicated that except for Disperse Blue 3, each of the remaining four dye standards contains essentially one major component, as illustrated in Figure 1. The Disperse Blue 3 dye standard was found to contain three major components, including HEMA (Figure I, III), which is commonly called Disperse Blue 3. The remaining two major components are structurally related to HEMA (see Figure 4) and are most likely byproducts from the synthesis of HEMA.

Similar analytical methodologies were used to characterize the four colored smoke mixes (red, yellow, green, and violet) before and after combustion as smoke grenades. The smoke mixes actually used in the smoke grenade formulation, were characterized first. The tentative identities and weight percentages of most components (> 0.1% by chromatographic area) in these smoke mixes were determined. More confident identities of major components were assigned using supporting spectroscopic data and chromatographic retention times. Results showed that red, yellow, and violet smoke mixes contain virtually the same components as their respective dye standards and that the green smoke mix contains 68% of Solvent Green 3 and 26% of Solvent Yellow 33.

The M18 grenades obtained from the JSABRDL were detonated in separate tents. Sampling ports for the collection of volatile and semivolatile materials on Tenax and XAD-2 resins, respectively, were made through the walls of the tents. Samples for particle size determination using a cascade impactor were also obtained through similar sampling ports. Particulate matter for chemical analysis was collected on a fiberglass extraction thimble within a stainless steel holder using a high volume sampling pump. In addition, glass trays were placed on the floor of the tent to catch particulate fallout in larger quantities (usually several grams).

The combustion experiments for the green, yellow, and violet grenades resulted in the formation of characteristic colored smokes, and the collection of fluffy, dry particulate material, as expected. A total of nine red grenades from two different lots were detonated and in not one of these experiments was a "normal" smoke obtained. In these detonations, an inordinate amount of flaming was observed from the base of the grenade, followed by the generation of grayish smoke. The particulate matter collected was also very dark in color. Because of the unusual smoke produced, the material collected was not thought to be characteristic of a typical red grenade. Particulate matter from an early run which did produce a slightly red smoke was chemically characterized; however, the results from these analyses are for informational purposes only and may not be representative of the materials usually formed from the red smoke grenades from a normal, combustion. [NOTE: A third lot of red grenades was successfully tested after the initial report was written. The results from this successful test are given in Appendix D. The composition of the combusted particulates did not differ qualitatively between these tests, only quantitatively.]

The particulate matter collected from both the high volume sampler and fallout was first extracted separately with methylene chloride, followed by chromatographic separation and spectroscopic analysis in the manner similar to the original smoke mixes. In order to evaluate any change in composition which may occur due to combustion, the uncombusted smoke mix (made by combining two smoke mixes, where necessary) was analyzed along with the combusted particulate samples to serve as control samples. Results indicated that the major components in the combusted particulates were unaltered original dyes. Minor components detected were decomposition products resulting from the combustion of the original dye. It was noted that the red and the violet smoke mixes appeared to undergo more chemical transformation than the green and yellow smoke mixes. 2-Methoxyaniline, naphtho-(1,2-d)-oxazole, 2-naphthol, and methoxyphenyl-naphthol were observed in the particulates from the red grenade. These are most likely degradation products from MBN. The violet smoke mix yields a number of anthraquinone-based degradation products, which are most likely formed from DMA (because it is a major component of the violet smoke mix), but might also arise from any of the three blue dyes. Two of those compounds, aminoanthraquinone and 1,4-diaminoanthraquinone have been shown previously to exhibit bacterial mutagenicity, although

these compounds are present at relatively low levels (a few percent). The other components produced from the violet smoke mix and red smoke mixes may also be bioactive.

Vapor phase samples, including volatiles and semivolatiles were tentatively identified by GC/MS, as described in Appendix A. Hexanes, benzene, C₂-benzene, cyanobenzene and hexadecane were major components (> 5% of chromatographable material) in the volatile materials isolated by Tenax resin traps from all four types of grenades. The semivolatile components (from XAD-2 resin traps) observed from the yellow grenade resemble those observed from the green trap, with naphthalene and C₂-styrene being the predominant components (13% by chromatographic area). Semivolatile components in the extracts generated from the red and violet XAD traps were mainly hydrocarbons, phthalates and esters of aliphatic acids.

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APPENDIX A

CHARACTERIZATION OF VOLATILES AND SEMIVOLATILES

APPENDIX A

Characterization of Volatiles and Semivolatiles

For the analyses of semivolatile components which had been collected on XAD-2 tubes, about 7.5 g of resin was transferred to a prewashed cellulose thimble and extracted with 500 mL methylene chloride for 16 hours. Solvent was evaporated from the extract under a stream of nitrogen, and the residue was dissolved in 1 mL methylene chloride. For analysis of these extracts by GC/MS, the GC column temperature was initially held at 35°C for 10 min, then programmed to 280°C at a rate of 4°C/min. The blank air sample collected on XAD-2 trap prior to grenade combustion was analyzed in the same manner.

To analyze the volatile components adsorbed on Tenax tubes, an approximately 250 mg portion of this Tenax resin was transferred to a prewashed stainless steel tube (4.5 mm ID x 21 cm). The tube was first purged at room temperature with helium at a rate of 100 mL/min for 10 minutes to remove moisture. The tube was then heated in a tube furnace at 243°C for 20 minutes under a helium flow (at a rate of 10 mL/min) to desorb the volatile components directly into the GC/MS. A loop of stainless steel tubing (0.5 mm ID x 46 cm) immersed in a liquid nitrogen Dewar flask was used prior to GC column to trap the desorbed volatiles and focus them at the head of the column. At the end of the 20 min desorption period, the liquid nitrogen Dewar flask was removed from the loop and temperature programming of the GC column was started. The column temperature was initially held at 25°C for 16 minutes, then raised to 280°C at a rate of 8°C/min. Blank air samples collected on the Tenax traps prior to grenade combustion were analyzed using the same procedure as described above.

Figures A-1 to A-5 illustrate the reconstructed GC/MS chromatograms of the vapor phase materials adsorbed on Tenax traps for the four combusted colored smoke grenades and an air blank sample. The profiles for the four combusted smoke grenades were different with respect to the relative quantities of materials present; however, the mass spectra of these components indicated that qualitatively the major volatile components of each grenade were nearly the same. Table A-1 lists the tentatively identified components found at levels greater than 1% of the total volatile material. Components, such as hexane, benzene, C₂-benzene, cyanobenzene, hexadecane, indene, acetophenone, quinoline, styrene, C₂ to C₄-cyclohexanes and C₂ to C₄-cyclopentanes were present in all four combusted samples. Each of the first five components represent more than 5% of the total volatile material. Some components, unique to the individual dyes, were also detected by MS. For example, methoxyaniline and phenylisocyanate, presumably decomposition products from Solvent Red 1 (MBN), were found only in the combusted red grenade.

While analyzing the extracts generated from the XAD traps, it was observed that components trapped from the combustion of yellow grenades

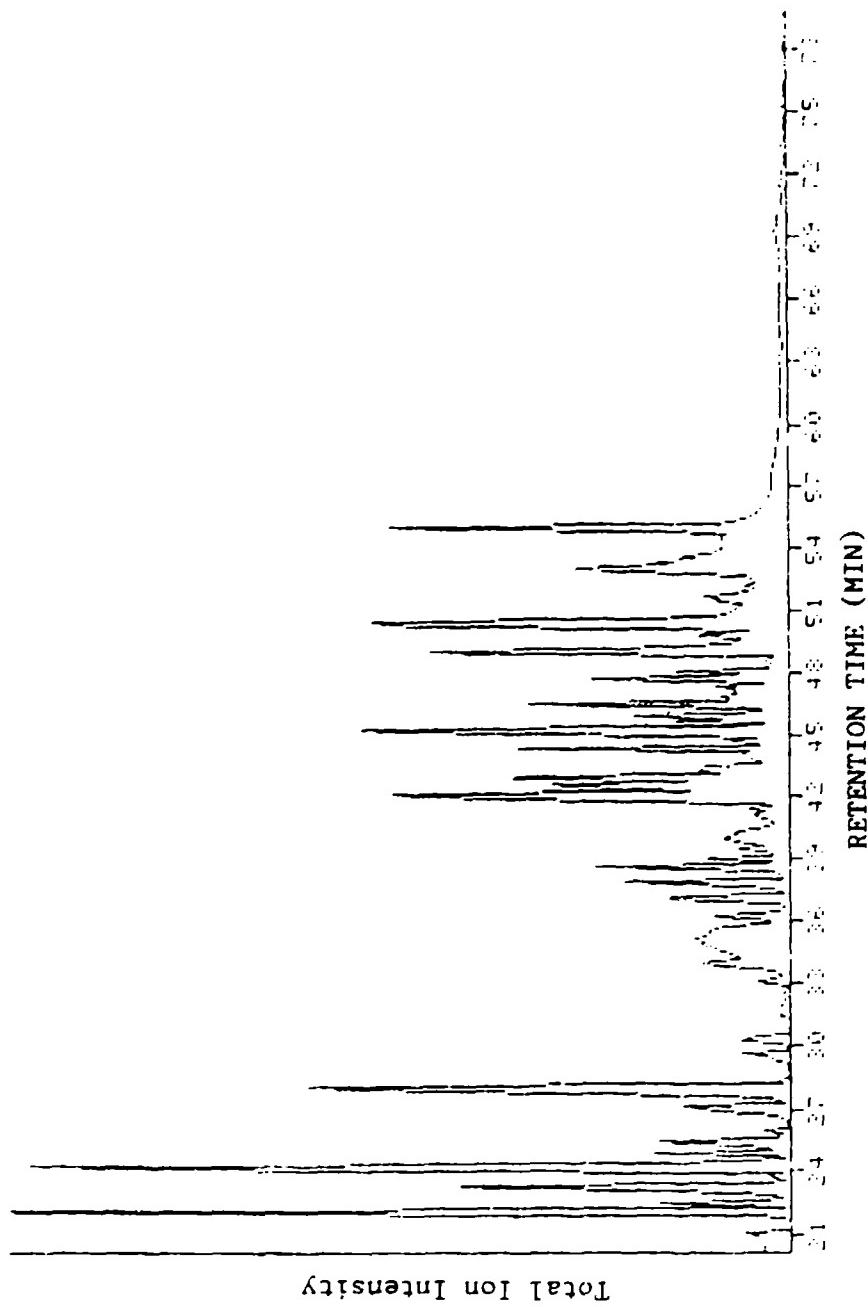


Figure A-1. Reconstructed GC/MS Chromatogram of Yellow Grenade Volatiles Trapped on Tenax

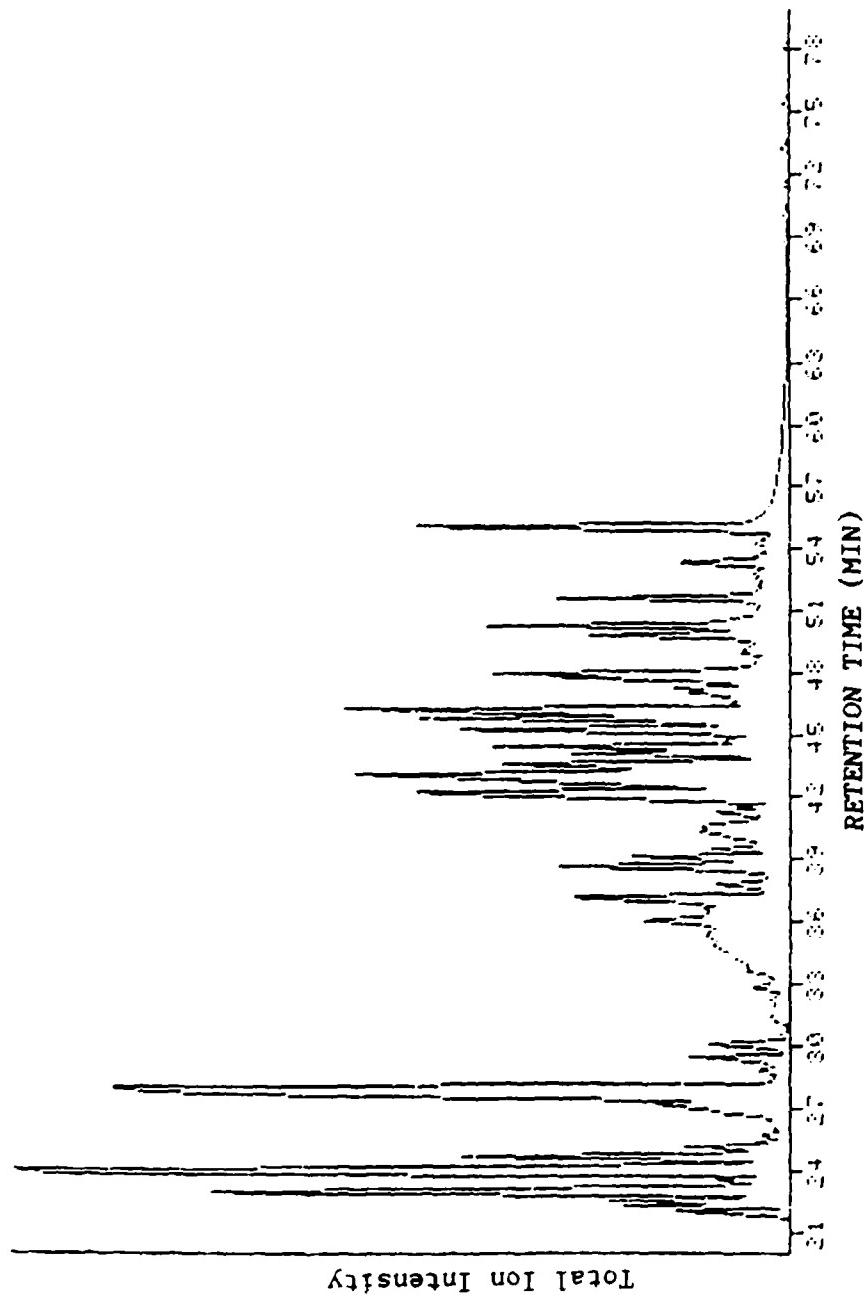


Figure A-2. Reconstructed GC/MS Chromatogram of Green Grenade Volatiles Trapped on Tenax

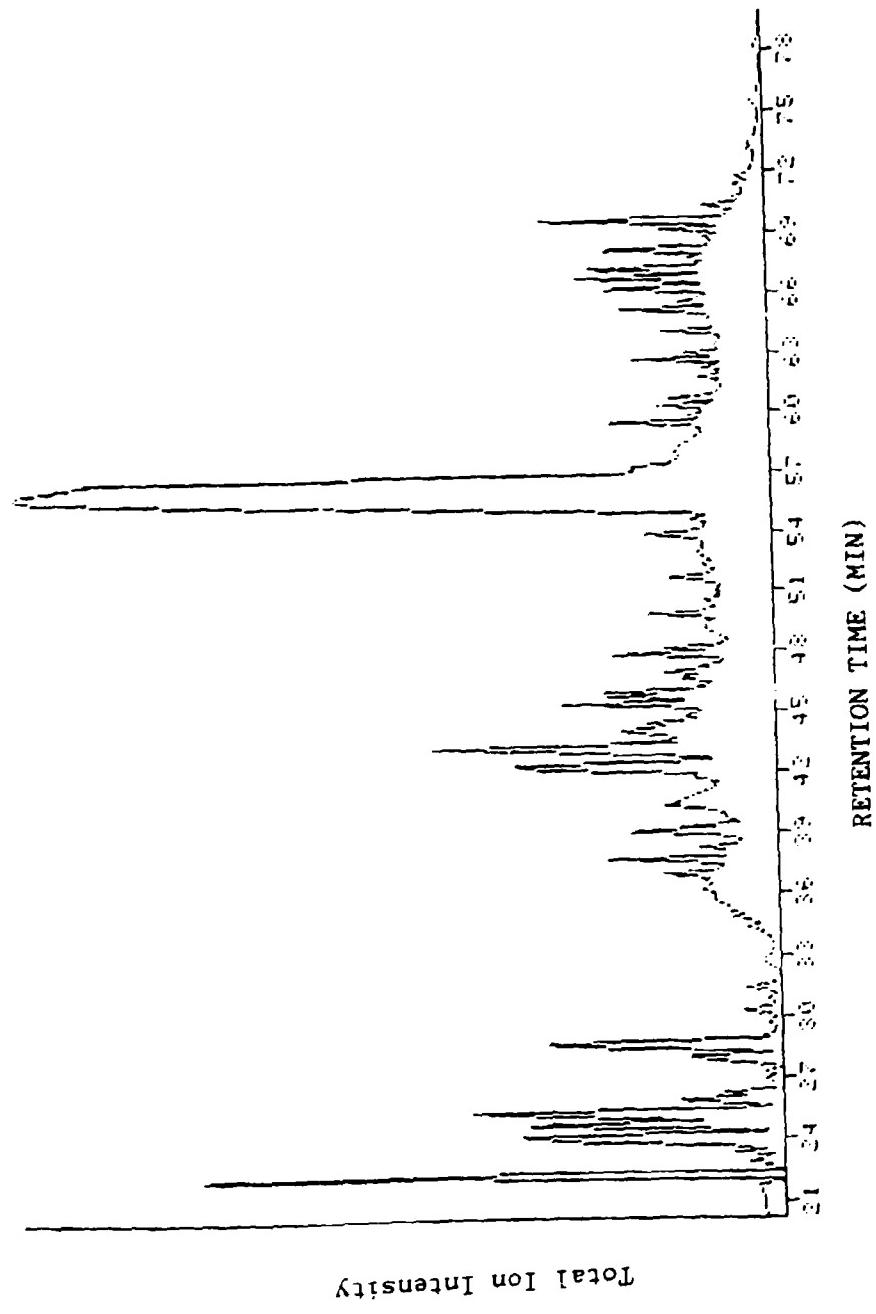


Figure A-3. Reconstructed GC/MS Chromatogram of Violet Grenade Volatiles Trapped on Terax

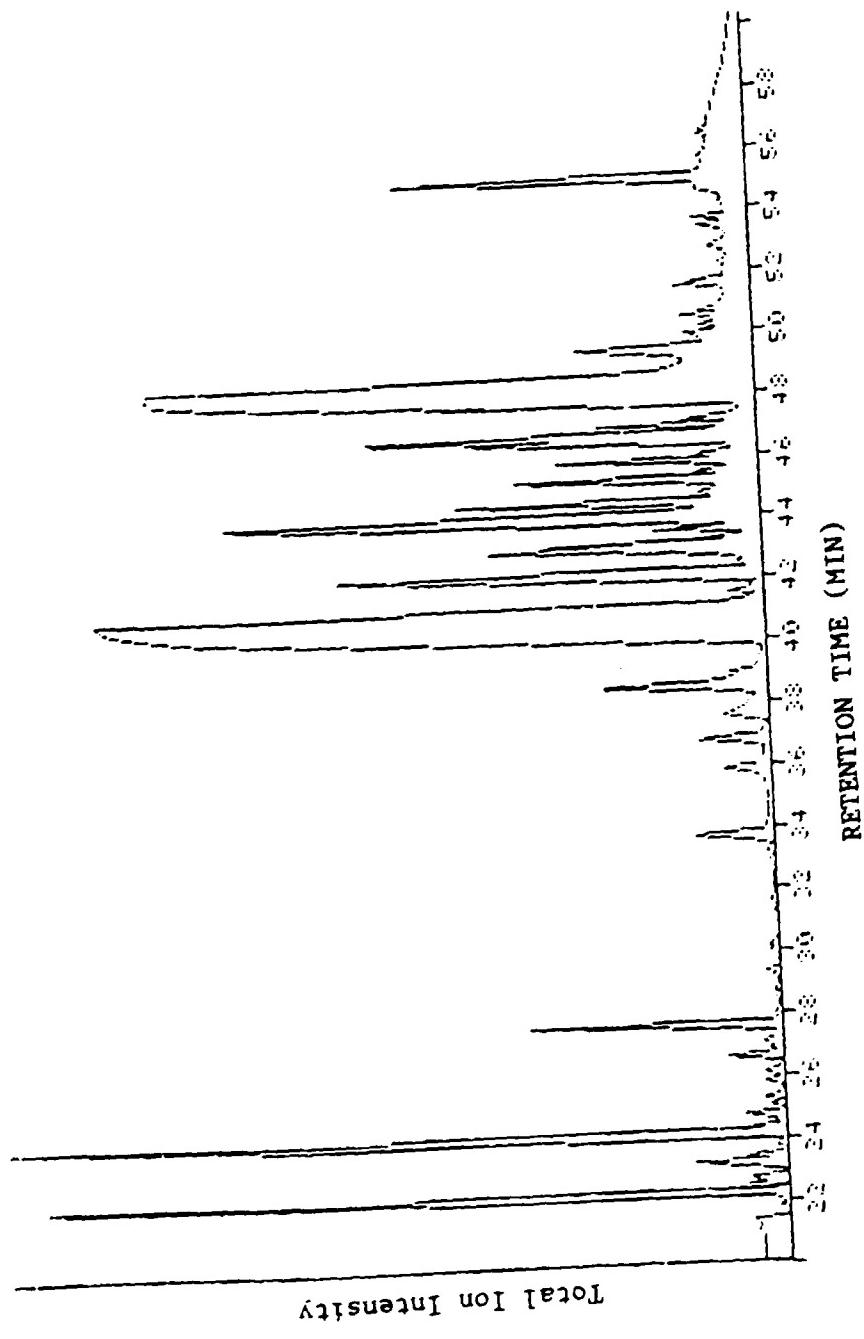


Figure A-4. Reconstructed GC/MS Chromatogram of Red Grenade Volatiles Trapped on Tenax

Figure A-5. Reconstructed GC/MS Chromatogram of Tenax Blank

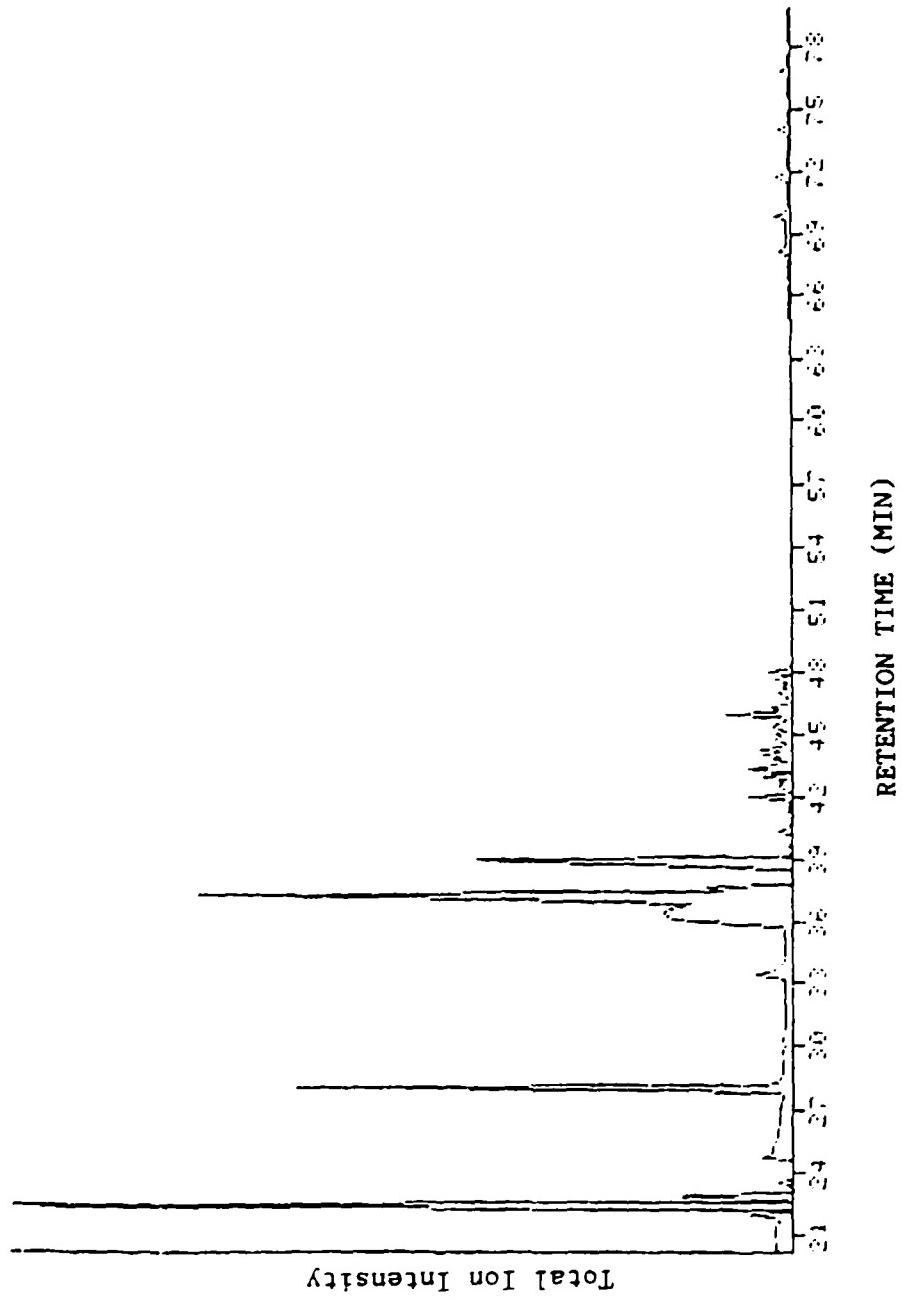


Table A-1. Volatile Components Collected on Tenax Traps*

	Green Grenade	Yellow Grenade	Violet Grenade	Red Grenade
benzene	C ₀ , ** C ₃ , cyano, *** C ₁ 2	C ₀ , ** C ₂ , ** cyano	C ₀ , ** C ₁ , ** cyano*** C ₂ , ** cyano***	C ₀ , ** C ₁ , C ₂ , ** isocyanato (or cyano-phenol)***
cyclopentane	C ₀ , C ₂ , C ₃ , C ₄	-	C ₀ **	-
cyclohexane	C ₄	C ₄	-	-
hydrocarbon	C ₆ , ** C ₁₆	C ₁₆ **	C ₆ , C ₁₆ **	C ₁₆
styrene	C ₀	C ₀ , C ₁	C ₀	C ₀
indene/C ₁ -phenylacetone	C ₀	C ₀	-	C ₀
Phenol	-	-	-	C ₁ ** (or n. toxybenzene)
acetophenone	C ₀	C ₀	C ₀	C ₀
quinoline	C ₁	C ₀ , C ₁ **	-	C ₀ **
miscellaneous compounds	C ₃ -furan butanone	phenylacetylene naphthalene phthalate ester	naphthalene benzofuran methoxyaniline	

*C_n represents number (n) of alkyl carbon substituents on parent compound.

**quantity greater than 5% of total chromatographic area, other components present at levels between 1 and 5%.

were similar to those trapped from the combustion of green grenades (Figures A-6, A-7). A list of these tentatively identified components is summarized in Table A-2. Components representing more than 1% of the total material include C₂-styrene, naphthalene, C₁-indene, C₅-benzene, biphenyl, C₃-styrene, C₆-disiloxane, C₁-naphthalene, C₄-phenylstyrene, C₆-phenylstyrene, C₈-diphenylstyrene and C₁₀-phenylstyrene, with the first two being the major components (each representing greater than 13%). XAD traps from the combusted red and violet grenades (Figures A-8, A-9) were found to contain C₁₀ to C₁₂ hydrocarbons, C₂ to C₄-cyclohexanes, phthalate esters and esters of aliphatic acids (Table A-2). However, numerous components such as biphenyl, methoxyaniline, C₂-methoxyaniline and C₄-pyridine were observed in the combusted red grenade. A GC chromatogram of the air blank sample collected on XAD trap is included in Figure A-10.

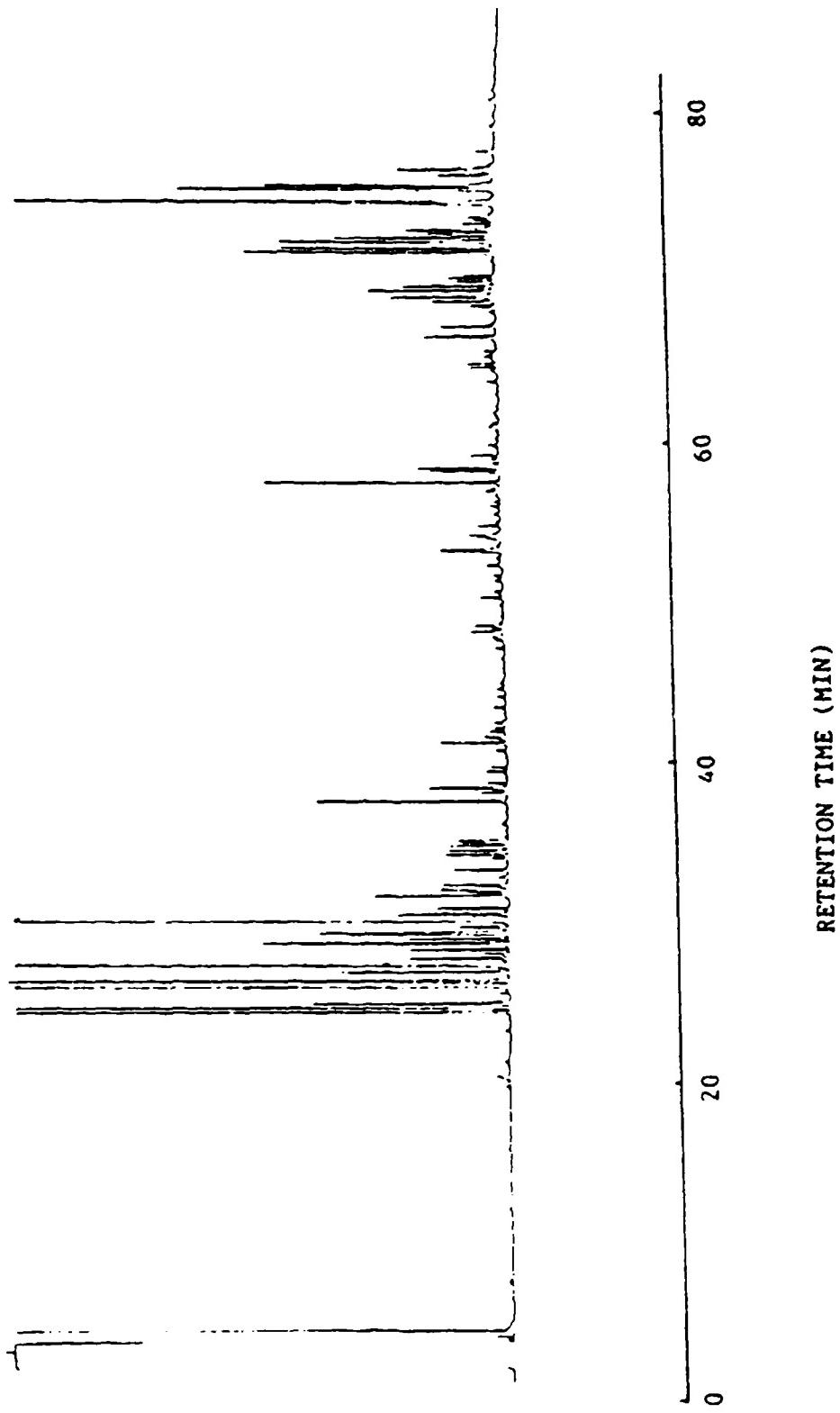


Figure A-6. Gas Chromatogram of Yellow Grenade Semivolatiles Trapped on XAD

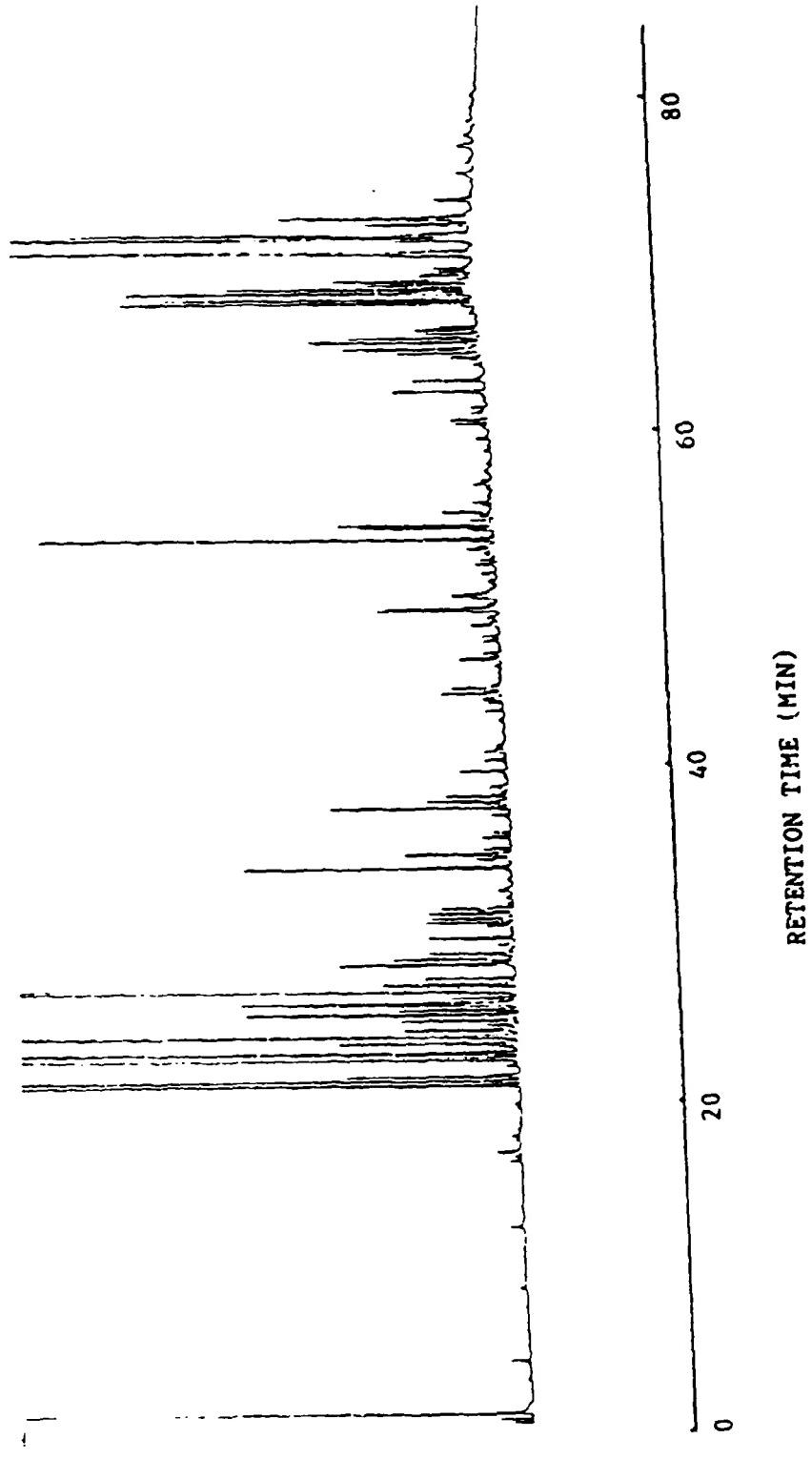


Figure A-7. Gas Chromatogram of Green Grenade Semivolatiles Trapped on XAD

Table A-2. Semivolatile Components Collected on XAD Traps*

	Green Grenade	Yellow Grenade	Violet Grenade	Red Grenade
styrene	C ₂ .** C ₃ .	C ₂ .** C ₃ .	-	-
phenylstyrene	C ₄ . C ₆	C ₂ . C ₄ . C ₆	-	-
diphenylstyrene	C ₈ .* C ₁₀	C ₆ . C ₈ .** C ₁₀	-	-
benzene	C ₅ . C ₆	C ₅ . C ₆	C ₄ . C ₅	-
naphthalene	C ₀ .** C ₁	C ₀ .** C ₁	-	-
biphenyl	C ₀	C ₀	-	C ₀
indene	C ₁	C ₁	-	-
phenol	C ₃	-	C ₄	C ₁
disiloxane	C ₆ . C ₇	C ₆ . C ₇	-	-
cyclohexane	-	-	C ₂ . C ₃	C ₃ . C ₄
hydrocarbon	-	-	C ₉ . C ₁₀ . C ₁₁	C ₁₀ . C ₁₁ . C ₁₄ . C ₁₆
miscellaneous compounds	-	-	C ₄ -acetate C ₈ -phthalate	C ₄ -pyridine (or C ₃ -aniline) C ₈ -phthalate C ₂ -benzoate methoxyaniline C ₂ -methoxyaniline triadecanoic acid ethyl ester pentadecanoic acid ethyl ester

*C_n represents number (n) of alkyl carbon substituents on parent compound.

**Quantity greater than 3% of total chromatographic area; other components present at levels between 1 and 5%.

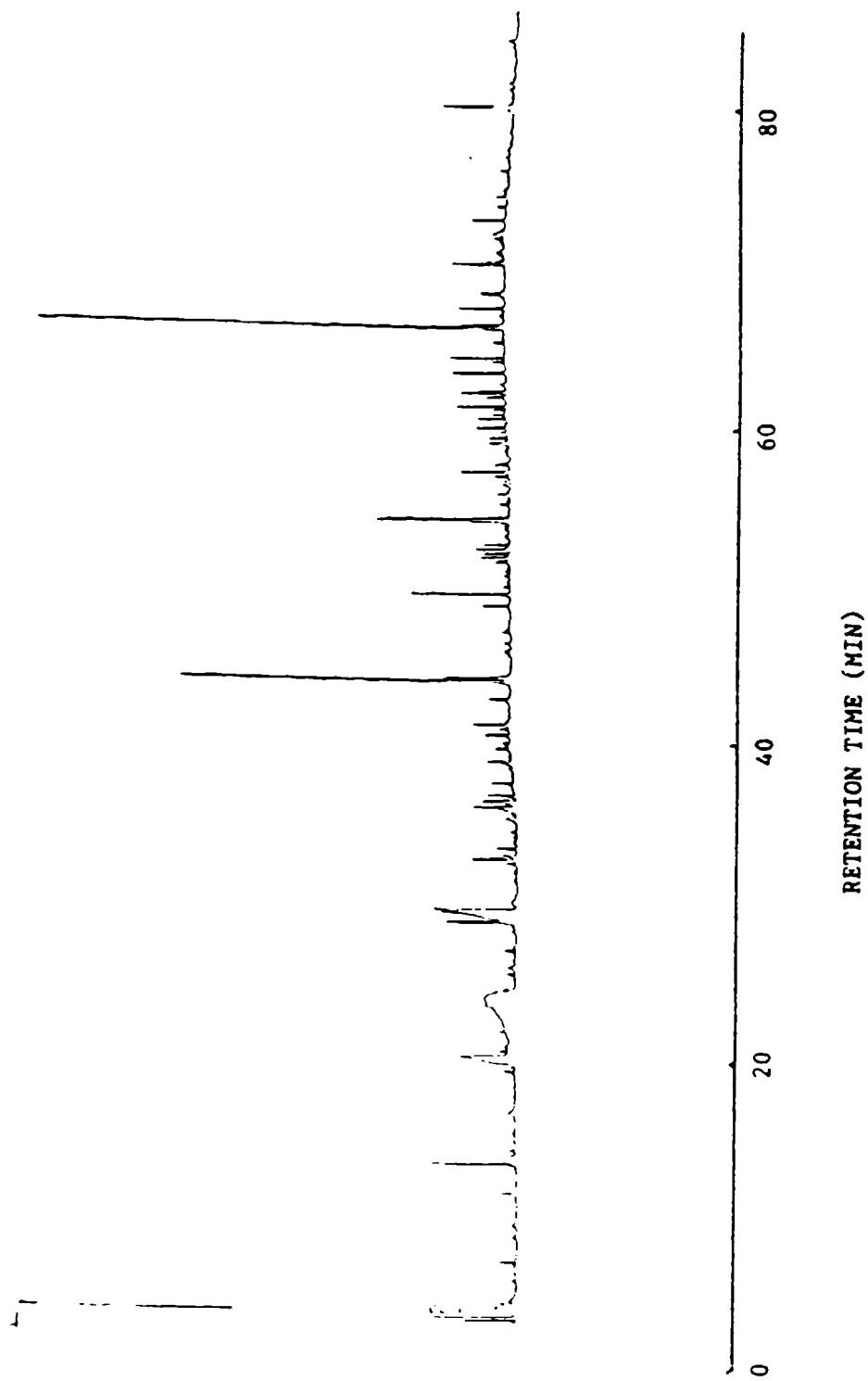


Figure A-8. Gas Chromatogram of Violet Grenade Semivolatiles Trapped on XAD

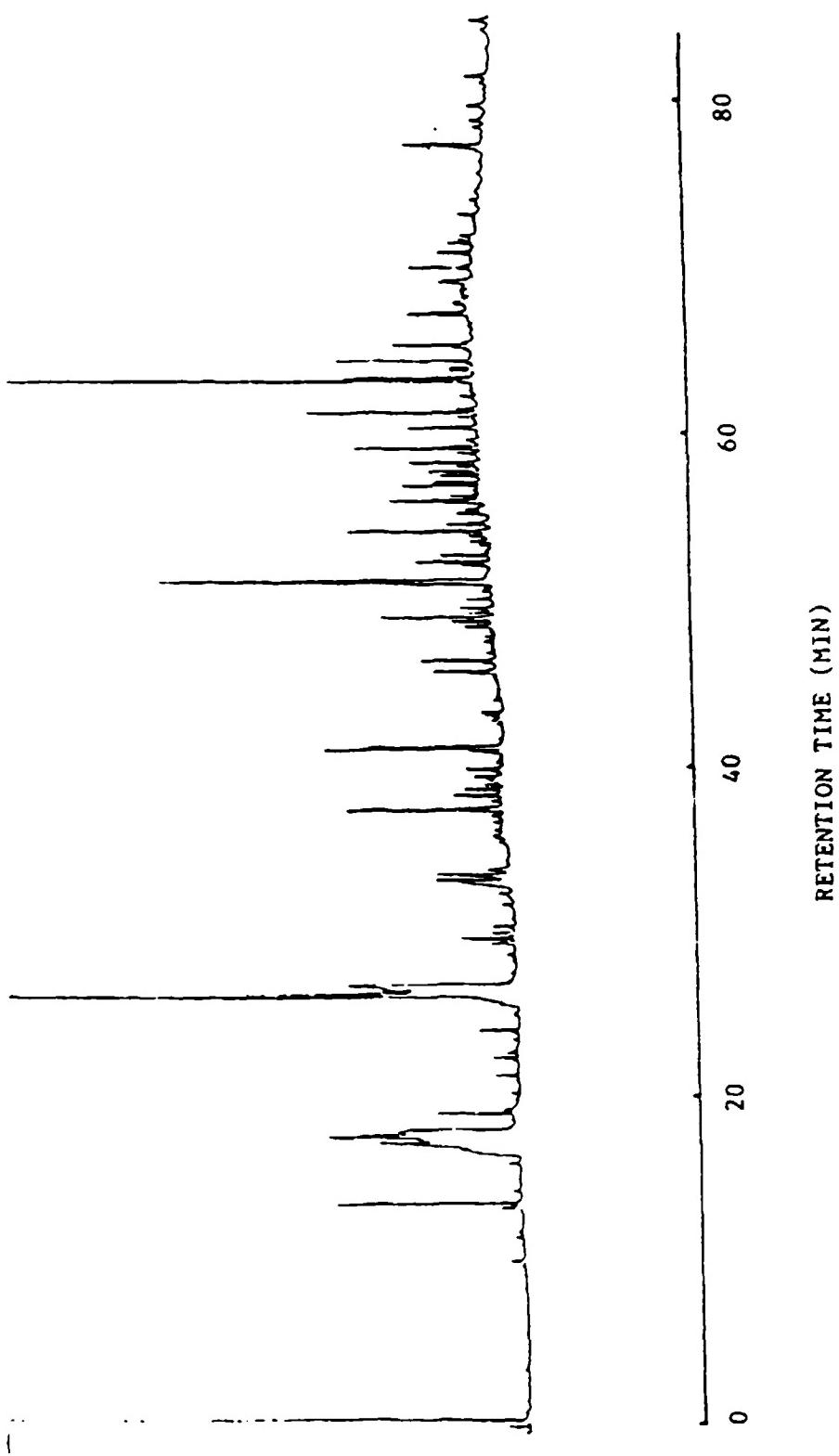


Figure A-9. Gas Chromatogram of Red Grenade Semivolatiles Trapped on XAD

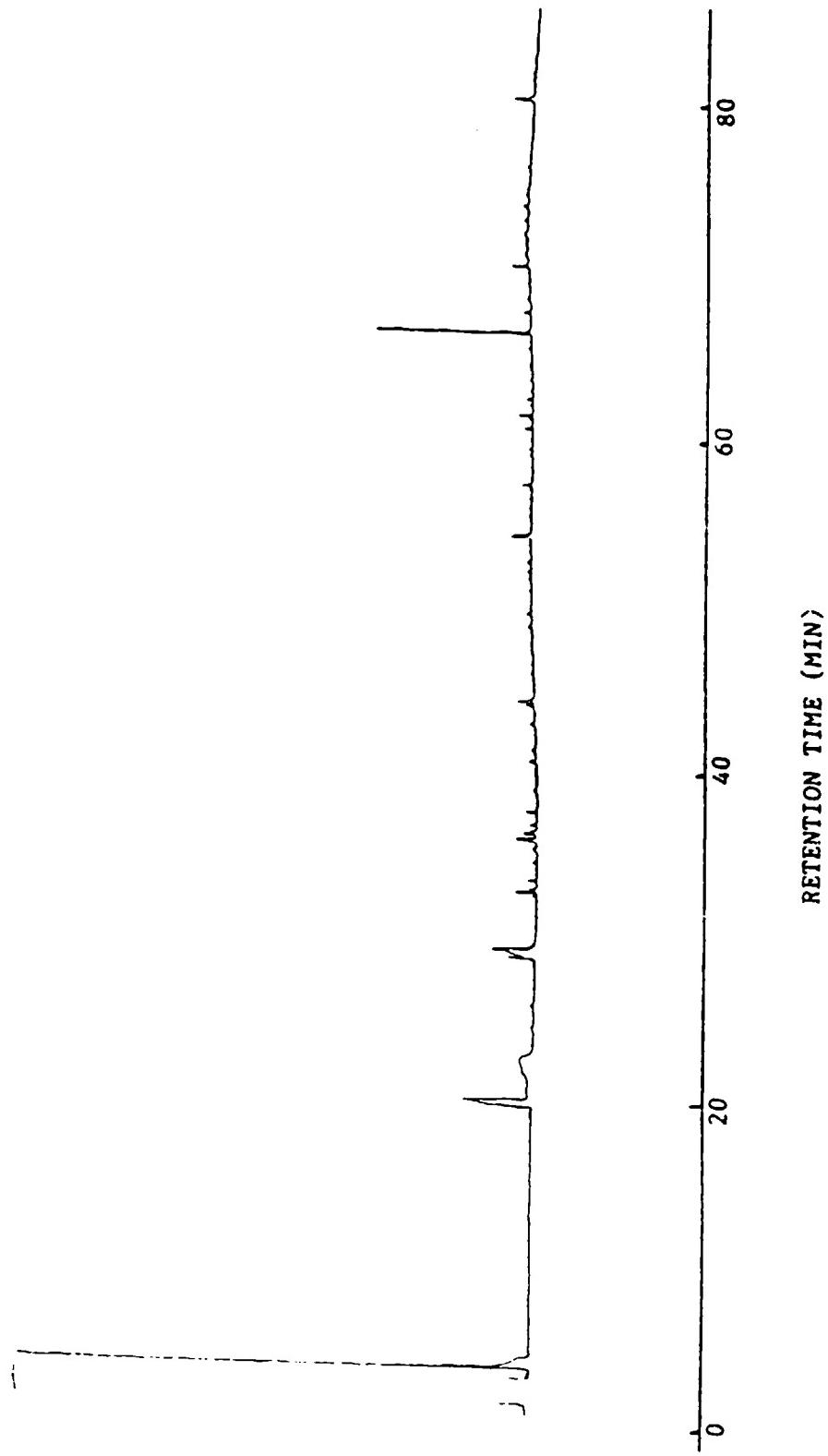


Figure A-10. Gas Chromatogram of XAD Blank

APPENDIX B

PARTICLE SIZE DISTRIBUTION

APPENDIX B

Particle Size Distribution

Figures B-1 to B-5 are the plots of log normal distributions versus aerodynamic diameters for four combusted colored smoke grenades. In all cases, the particle size distribution approaches a log normal distribution. The particle size was determined at both 3 and 30 minutes after the detonation. In general, the 30 minute sample is 50 to 100% greater in diameter than the 3 minute sample (Table 9). This behavior was expected due to particle aggregation as the aerosol ages.

Table B-1. Particle Size Determination of Combusted Smoke Mixes

	Aerodynamic Mass Median Diameter (μm)	Geometric Standard Deviation
"Abnormal" Red Grenade		
A*	2.30	1.52
B	3.45	1.46
"Normal" Grenade		
A	2.33	1.71
B	3.32	1.40
Violet Grenade		
A	1.40	1.70
B	2.70	1.65
Yellow Grenade		
A	0.85	1.90
B	1.80	1.61
Green Grenade		
A	1.57	1.75
B	2.05	1.76

*A series were collected at 3 minutes after ignition
B series were collected at 30 minutes after ignition

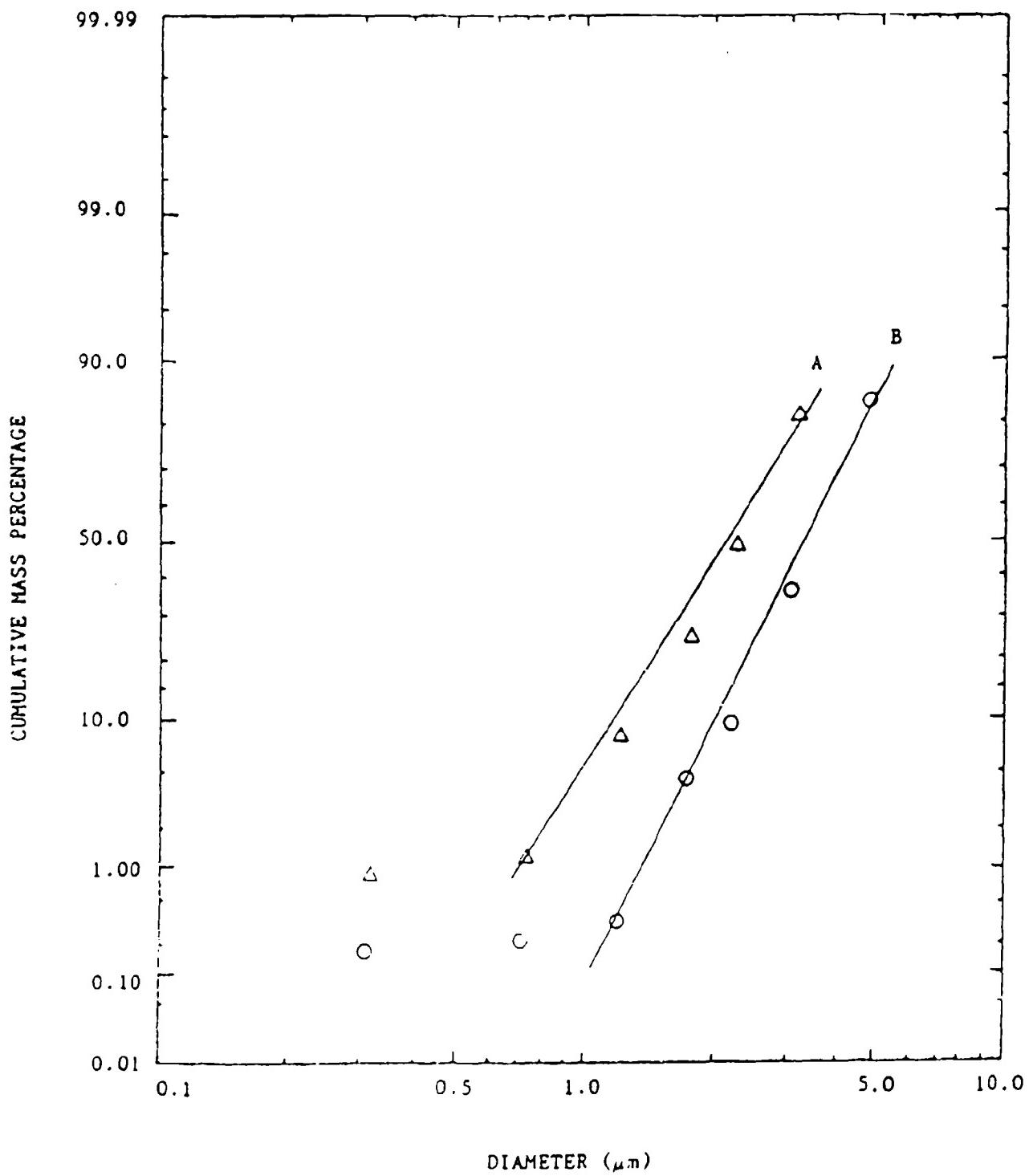


Figure B-1. Particle Size Analysis of Combusted Red Grenade
A. 3 Minutes After Ignition
B. 30 Minutes After Ignition

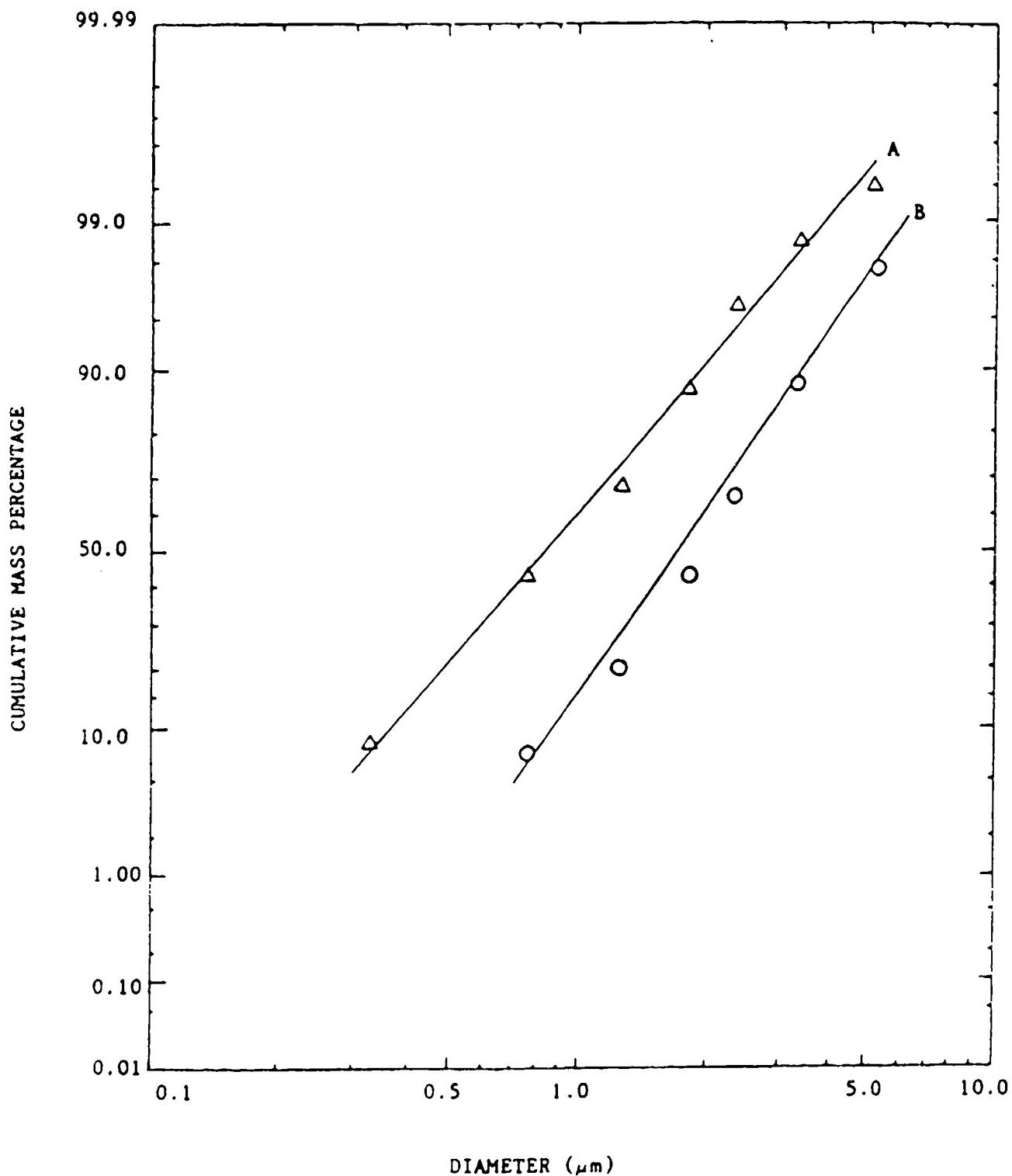


Figure B-2. Particle Size Analysis of Combusted Yellow Smoke Grenade
A. 3 Minutes After Ignition
B. 30 Minutes After Ignition

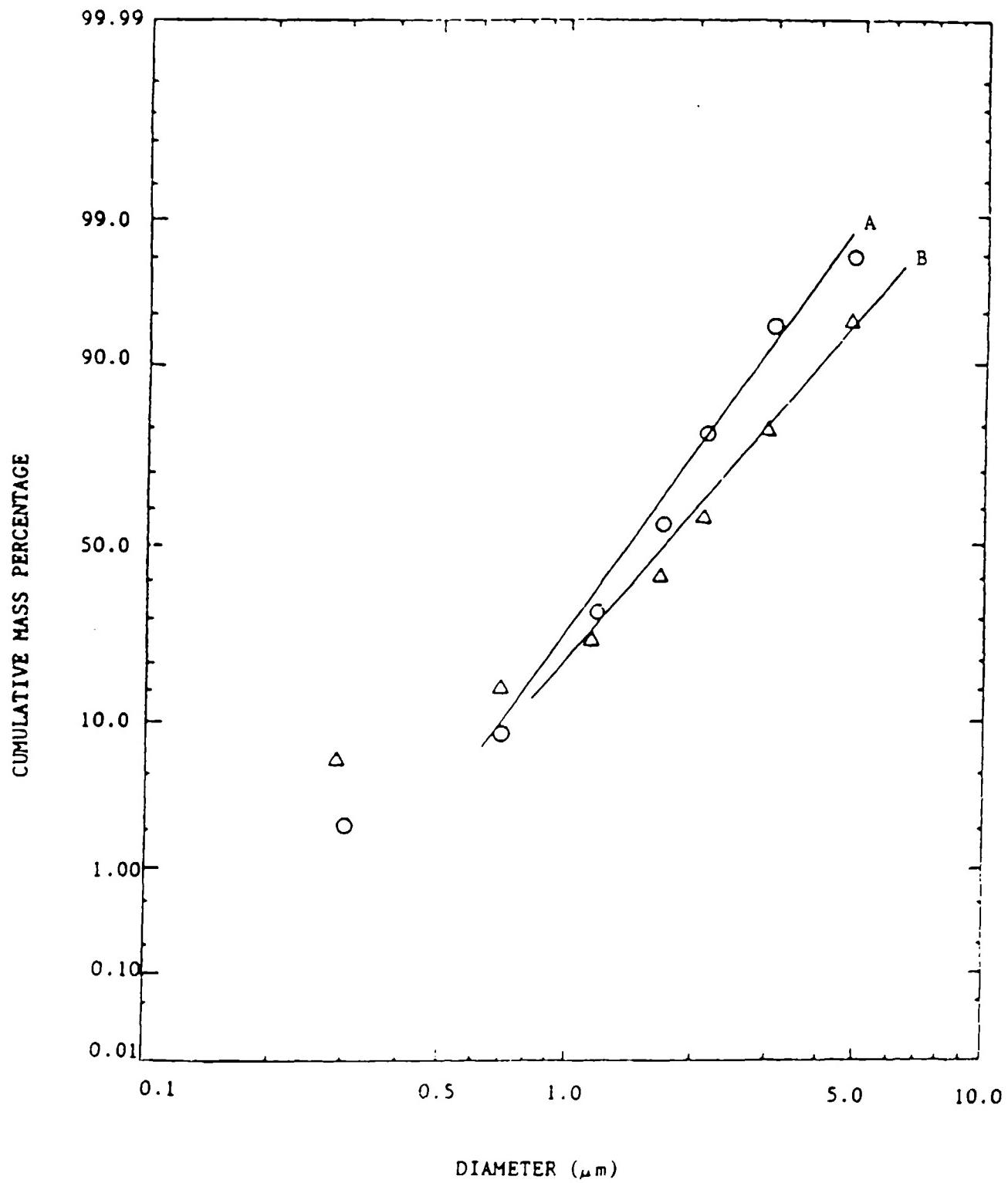


Figure B-3. Particle Size Analysis of Combusted Green Smoke Grenade
A. 3 Minutes After Ignition
B. 30 Minutes After Ignition

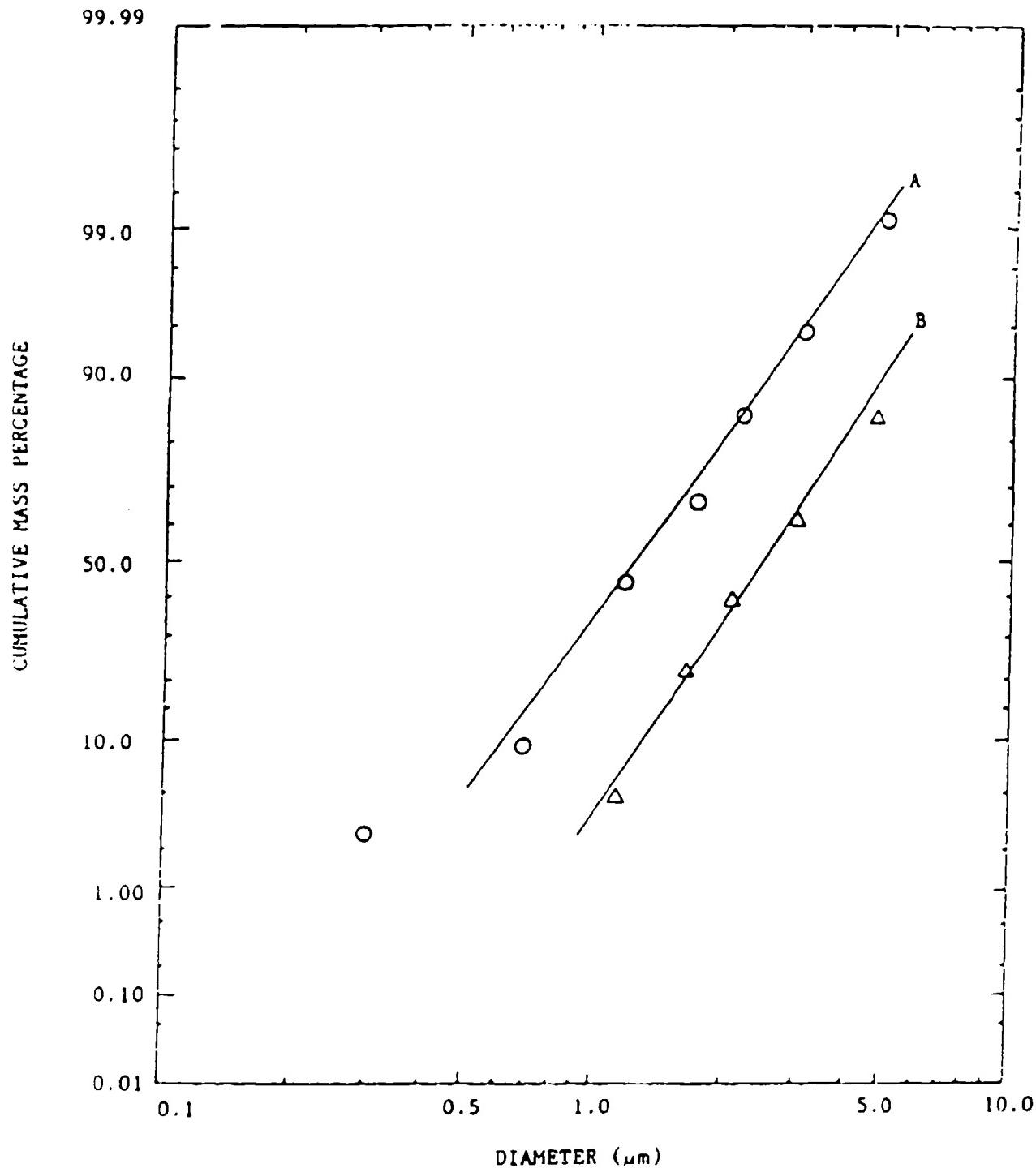


Figure B-4. Particle Size Analysis of Combusted Violet Smoke Grenade
A. 3 Minutes After Ignition
B. 30 Minutes After Ignition

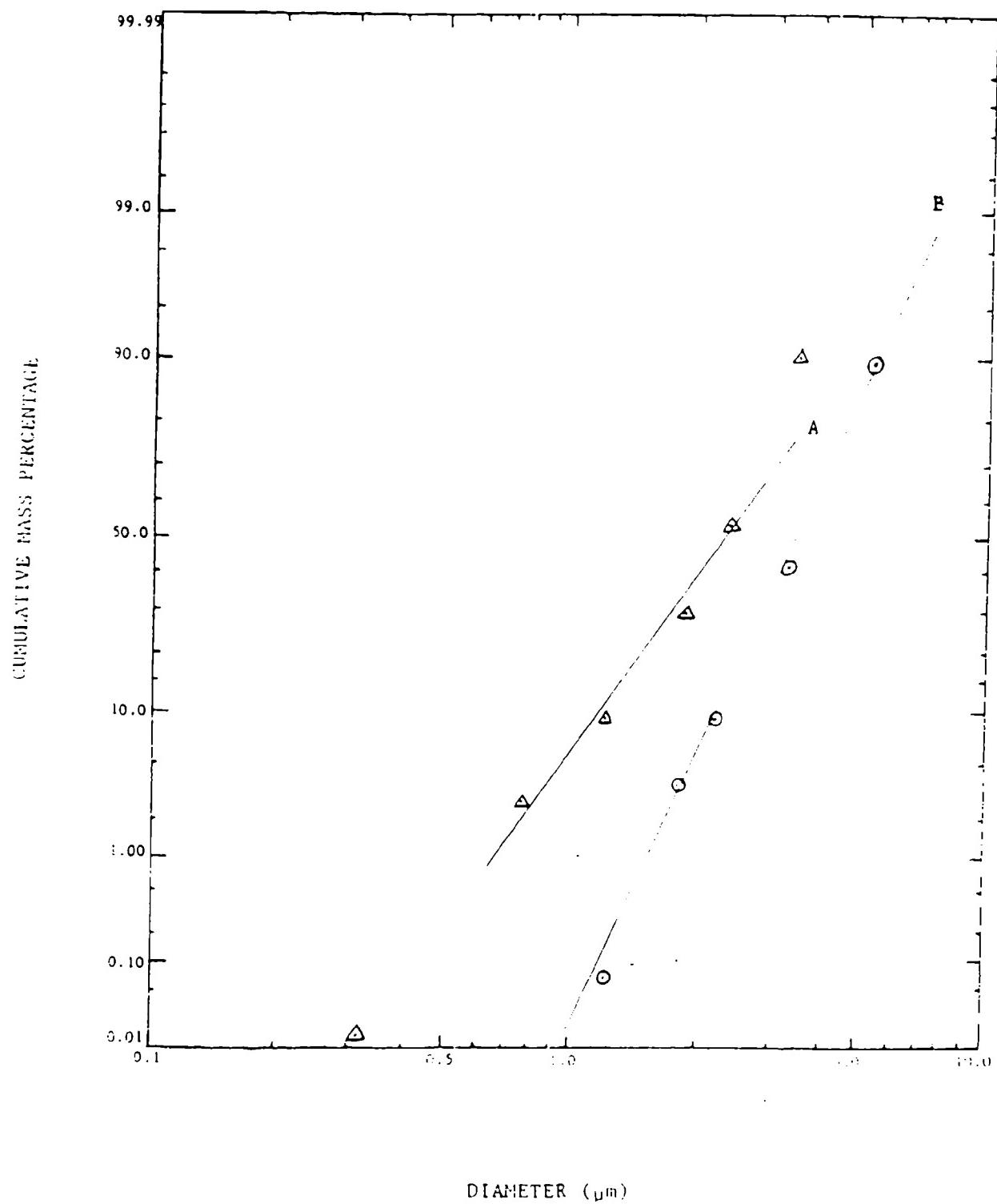


Figure B-5. Particle Size Analysis of Combusted Red Smoke Grenade from Third Lot

A. 3 Minutes After Ignition
 B. 30 Minutes After Ignition

APPENDIX C

UV/VIS SPECTRA OF SMOKE MIXES AND SMOKE PARTICULATES

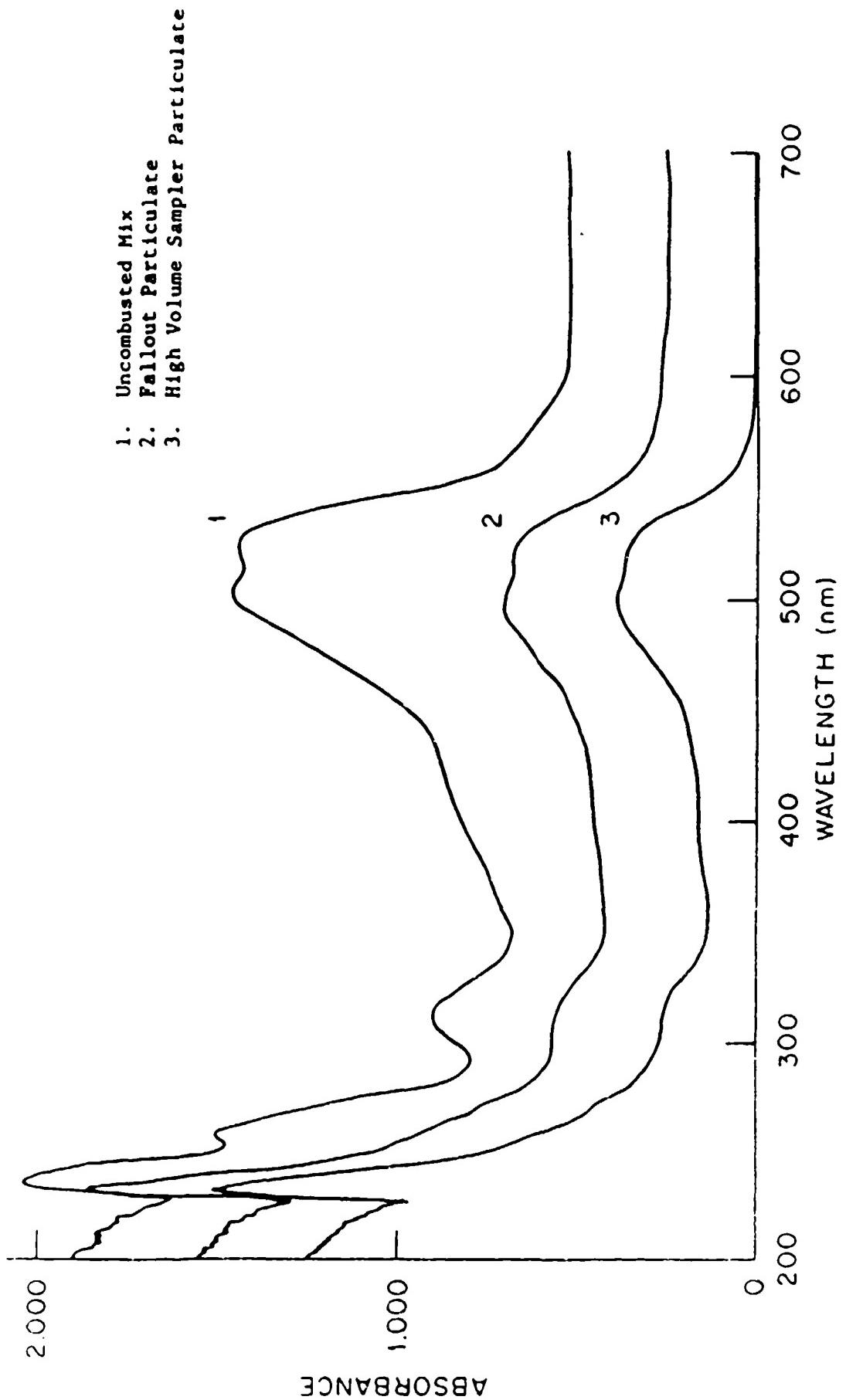


Figure C-1. UV/VIS Spectra of Red Smoke Mix and Particulates from Red Smoke Grenades

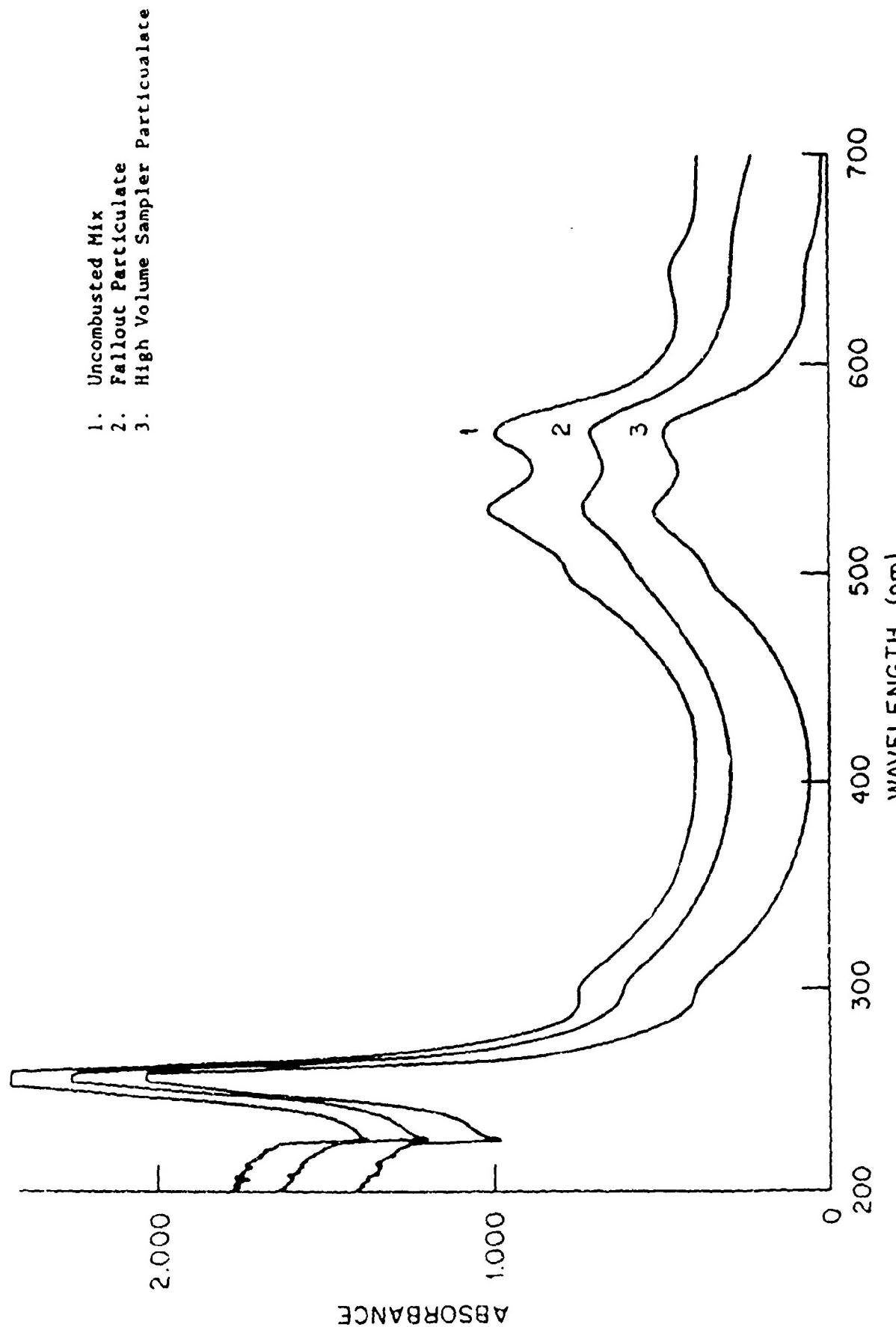


Figure C-2. UV/VIS Spectra of Violet Smoke Mix and Particulates from Violet Smoke Grenades

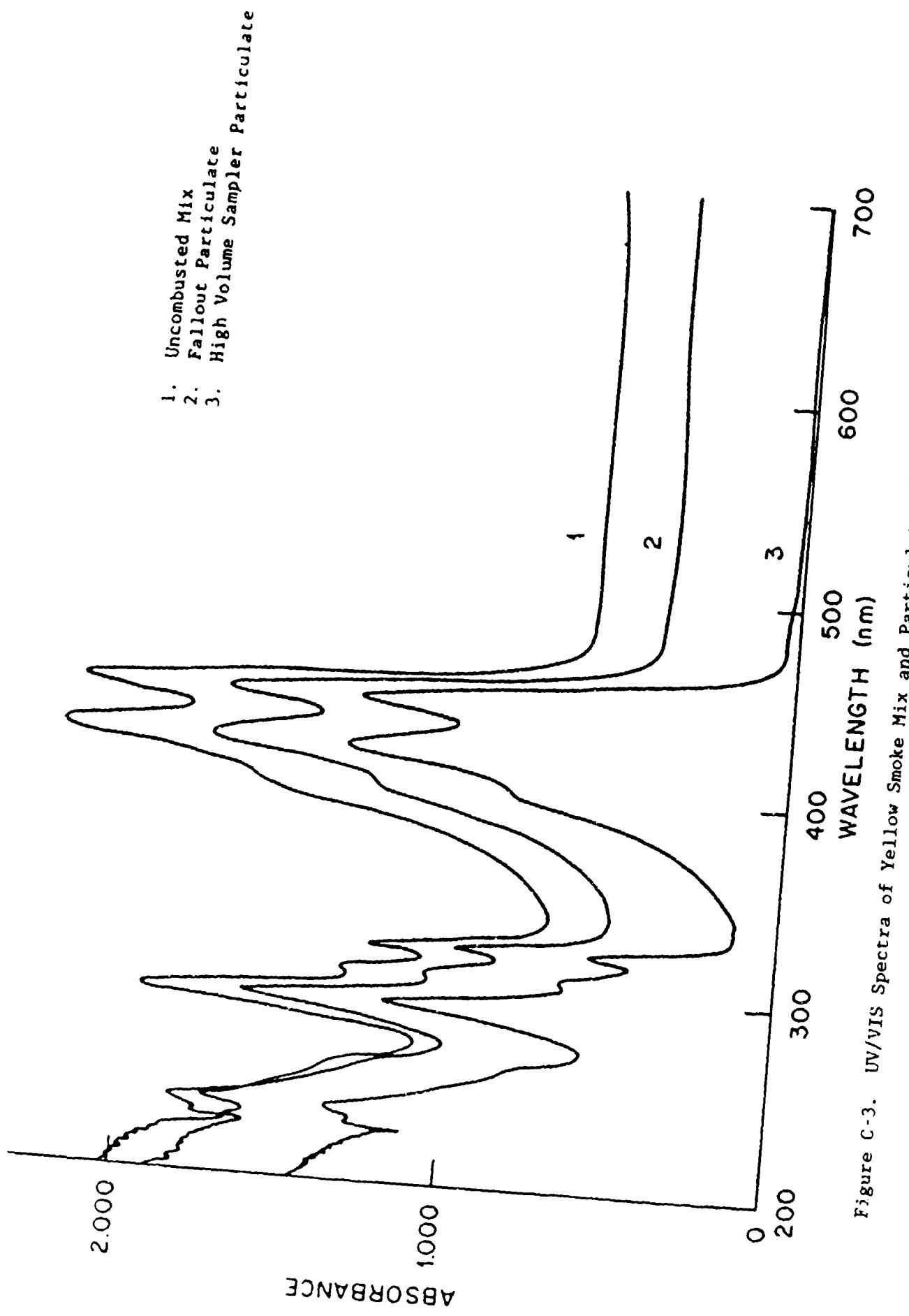


Figure C-3. UV/VIS Spectra of Yellow Smoke Mix and Particulates from Yellow Smoke Grenades

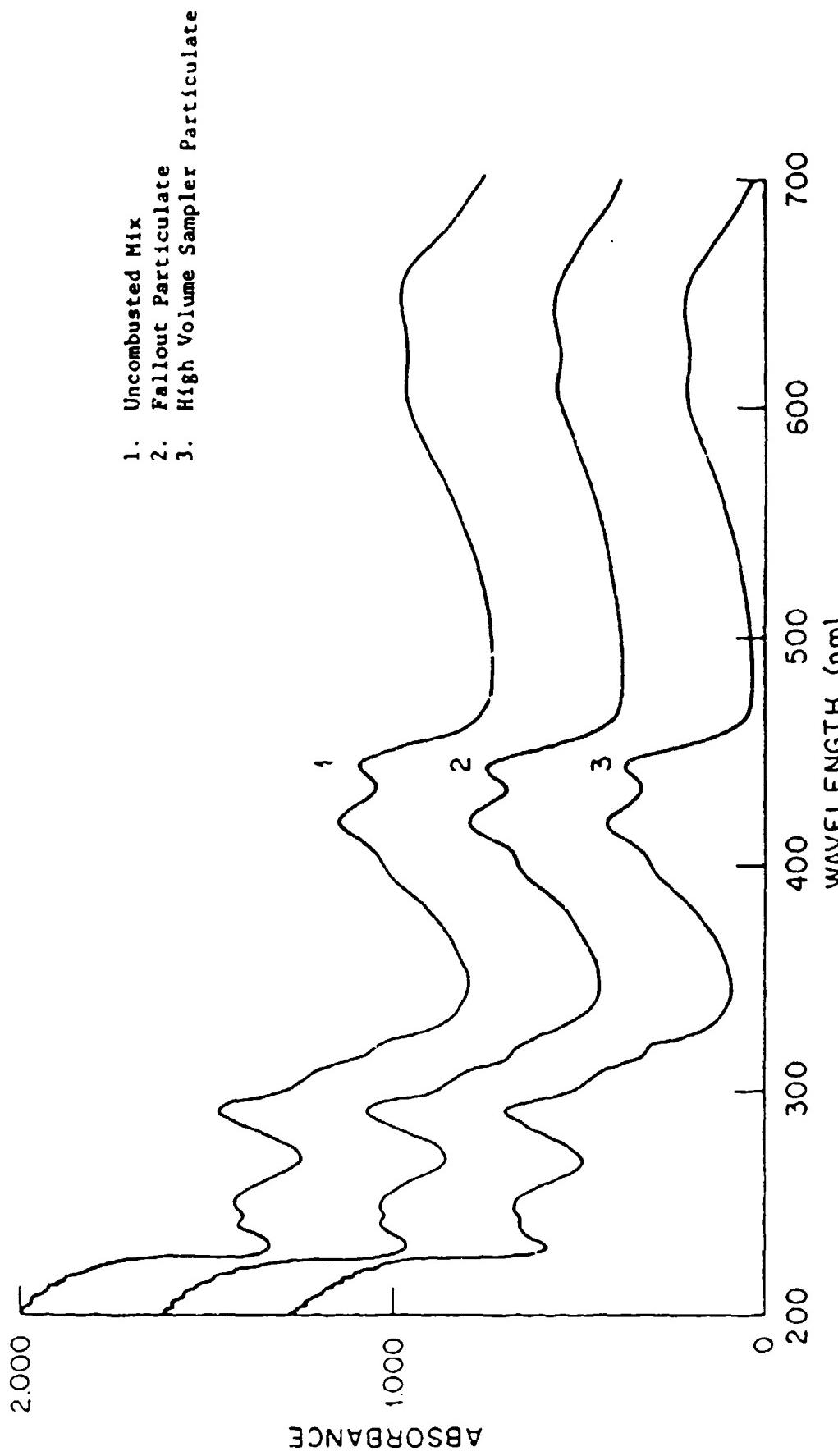


Figure C-4. UV/VIS Spectra of Green Smoke Mix and Particulates from Green Smoke Grenades

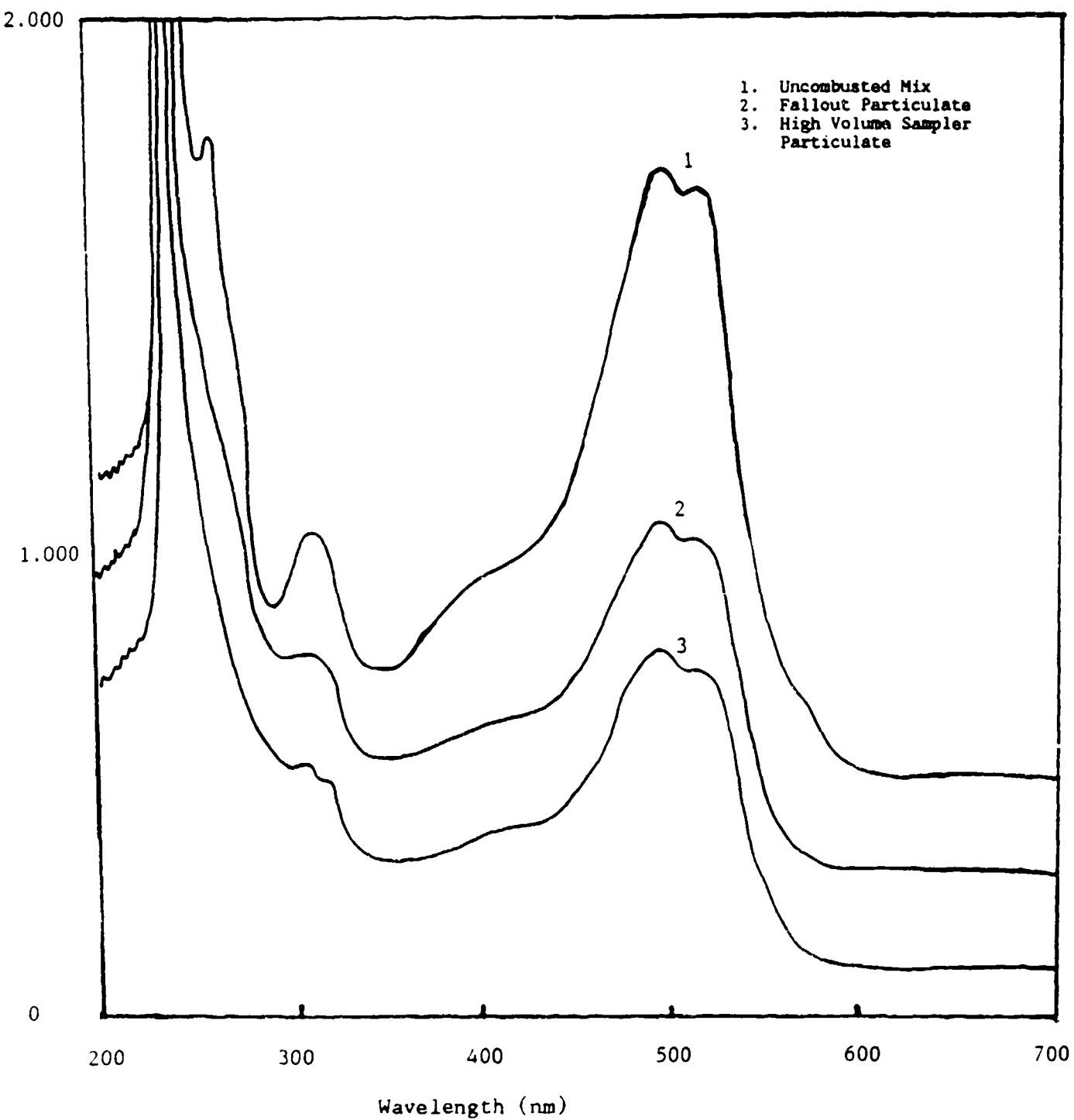


Figure C-5. UV/VIS Spectra of Red Smoke Mix and Particulates from Third Lot of Red Smoke Grenades

APPENDIX D

CHEMICAL CHARACTERIZATION OF RED SMOKE MIX
PARTICULATES AND VOLATILES FROM THIRD LOT OF GRENADES

APPENDIX D

A third lot of red smoke grenades were received on April 20, 1988. A combustion experiment was conducted with a single grenade on May 30, 1988. Unlike the experiments with the previous red grenades, this grenade produced large quantities of bright red smoke with virtually no flaming. A total of 5 g of particulates was obtained as fallout and 2.5 g from the HVS, which is considerably more than was collected with the previous grenades.

The particulates were extracted with methylene chloride and the major components were characterized as described previously using GC and low resolution GC/MS. In addition, a synthetic red smoke mix comprised of Solvent Red 1 and Disperse Red 11 was also characterized as a reference material. Table 10 summarizes the identification and weight distribution of the compounds in the red smoke particulates. The weight percentages of the components were determined by GC, using anthracene as an internal standard.

As indicated in Table D-1, the particulates from the fallout and the HVS were very similar. Both MBN and DMA were more confidently assigned on the basis of comparison of chromatographic retention times and mass spectra with the dye standards. Aminoanthraquinone, present in the red smoke mix, was not detected in the combusted particulates.

The remaining components were characterized in more detail by GC/FTIR, which was recently installed in our laboratory, and by laser desorption FTMS, which allows exact molecular weight information (i.e., exact elemental composition) to be obtained. A compound with a molecular ion at m/z 123 had been assigned as methoxyaniline in the previous red smoke particulates, with fragment ions at m/z 108, 92, and 80. Using GC/FTIR and FTMS, this compound was more confidently identified as 2-methoxyaniline (C_7H_9NO), a possible decomposition product from MBN upon combustion. Infrared bands were observed as follows: aromatic stretching at 3068 cm^{-1} and 3008 cm^{-1} ; aliphatic stretching at 2948 cm^{-1} and 2844 cm^{-1} ; amino N-H stretching at 3500 cm^{-1} and 3408 cm^{-1} ; alkyl-aryl ether stretching at 1266 cm^{-1} and 1619 cm^{-1} . Differentiation of positional isomers was achieved by matching the IR spectrum of this component with the spectra of ortho-, meta-, or para-anisidine in the spectral library, and it was found that the spectrum of this component (Figure D-1) was virtually identical with the spectrum of ortho-anisidine. A similar compound was assigned as C_2 -substituted methoxyaniline ($C_{11}H_{13}NO$). This component exhibits a molecular ion at m/z = 151 and fragment ions at m/z 123, 108, 92, and 80. GC/FTIR data also supported this assignment, with additional aliphatic C-H stretching observed at 2854 cm^{-1} , due to the alkyl group in the parent compound, methoxyaniline.

Naphthol was observed in the particulates from the original red smoke grenades. Using GC/FTIR and LD/FTMS, this compound was more confidently identified as 2-naphthol. This compound had a molecular ion at m/z 144, with an elemental composition of $C_{10}H_8O$ (measured

PEAK 1

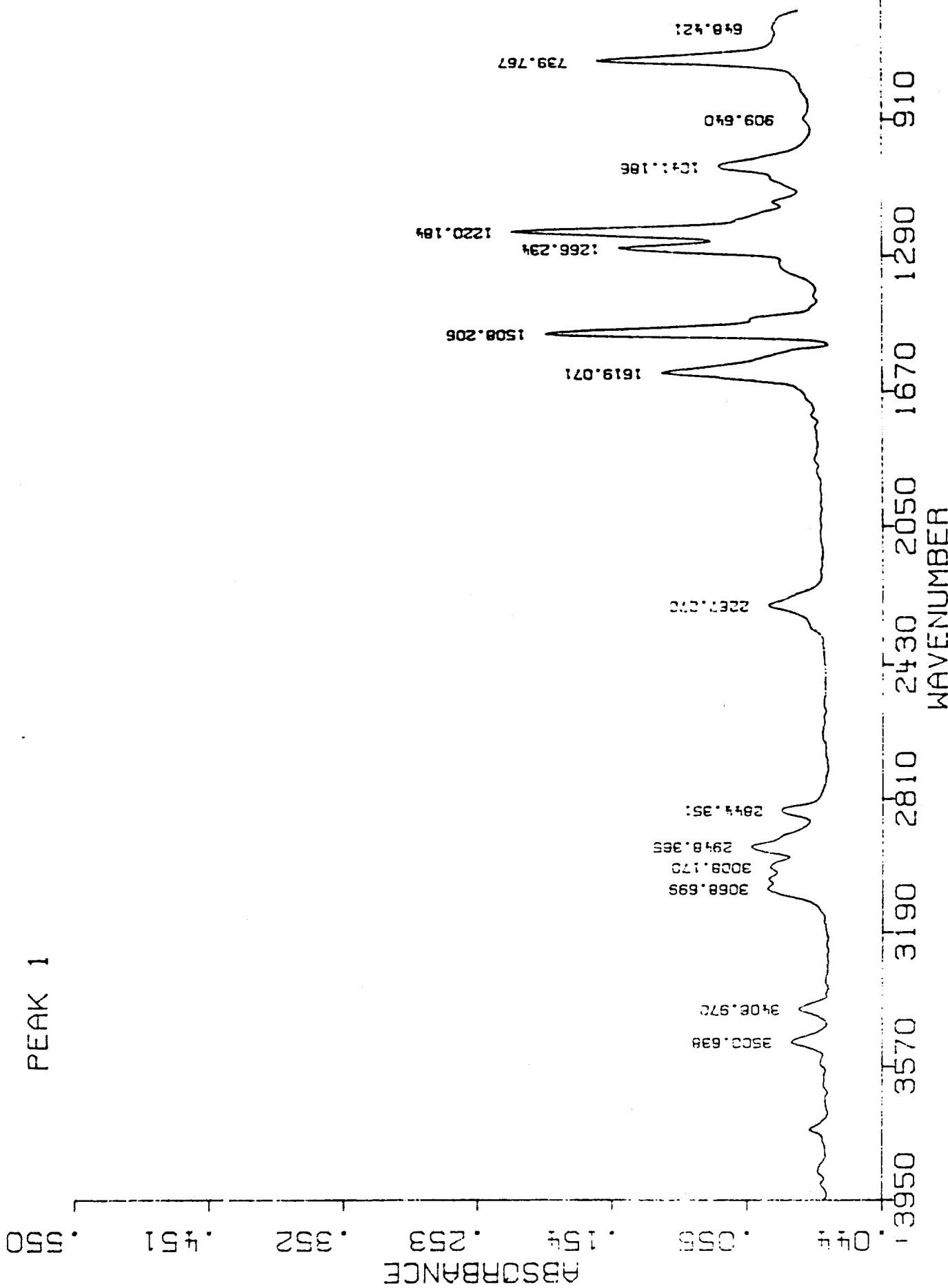


Figure D-1. IR Spectrum of Orthoanisidine Identified in Red Smoke Particulates by GC/FTIR

Table D-1. Composition of Red Smoke Grenade Particulates and Red Smoke Mix

Methylene Chloride Extractable	Weight % ^a				Relative Composition ^c	
	Smoke Mix	Combusted Particulates Fallout	HVS	Smoke Mix	Combusted Particulates Fallout	HVS
a-Methoxybenzene-azo-β-naphthol (MBN)	89	39	51	100	100	100
1, 4-Diamino-2-methoxyanthraquinone (DMA)	15	2	2	17	5	4
Aminoanthraquinones	<0.1	ND	ND	<0.2	ND	ND
2-Methoxyaniline	ND	4	12	-	10	24
C₂-Methoxyaniline	ND	<0.1	0.1	-	<0.3	0.2
2-Naphthol	ND	4	10	-	10	20
Naphtho(1,2-d)-oxazole	ND	4	16	-	10	31
C₁-naphtho-(1,2-d)-oxazole	ND	0.6	2	-	2	4
C₂-naphtho-(1,2-d)-oxazole	ND	<0.1	ND	-	<0.3	ND
C₃-naphtho-(1,2-d)-oxazole	ND	0.1	0.2	-	0.3	0.4
Phthalate ester	ND	<0.1	ND	-	<0.3	ND
Methoxyphenylnaphthol	ND	4	6	-	10	12
Total Extractable Material (wt%) ^b	98.4	94.9	89.3			
Residue (wt%) ^b	1.6	5.1	10.7			

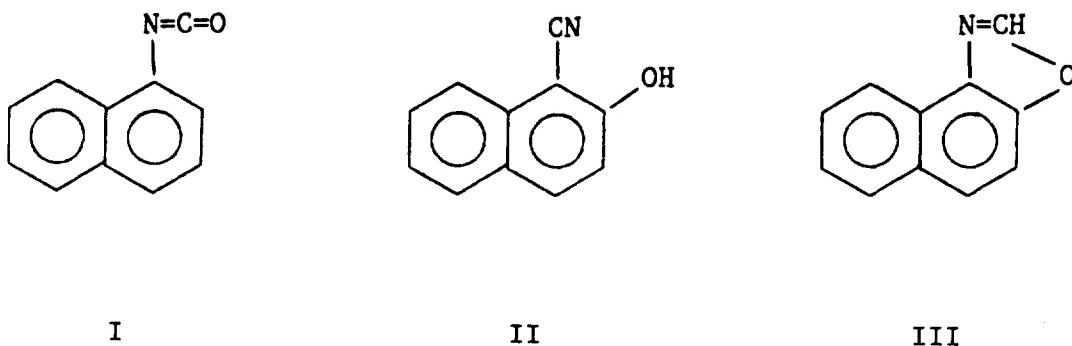
^adetermined by GC, wt% of the extractable material^bdetermined gravimetrically, wt% of the original material^ccalculated on the basis of the major component being set arbitrarily at 100%

bold type - tentative assignment; others confirmed by chromatography

ND = not detected

144.058, calculated 144.057), and fragment ions at m/z 126, 115, 116, 89, and 72. Infrared spectra further supported the assignment of this compound as 2-naphthol with absorption bands at 3563 cm^{-1} (O-H stretching); 3067 cm^{-1} (aromatic C-H stretching); 1512 cm^{-1} (aromatic in-plane vibration); and 1174 cm^{-1} (C-O stretching). In order to differentiate the positional isomers (1-naphthol or 2-naphthol), the IR spectrum of this component was searched against the gas phase spectra from the spectral library. It was found that the IR spectrum of this component (Figure D-2) matched well with that of 2-naphthol.

In the previous study of red smoke particulates, low resolution mass spectra yielded a predominant molecular ion at m/z 169 and minor fragment ions at m/z 141, 114, and 88. In the present characterization studies of the present smoke particulates, additional information was obtained using LD/FTMS and GC/FTIR to more confidently identify this compound. Results from high resolution LD/FTMS analysis indicated that this component possesses an elemental composition of $\text{C}_{11}\text{H}_7\text{NO}$ (measured molecular weight 169.062; calculated 169.052). Based on this information, three possible chemical structures could be postulated (shown below) which might have been derived from the decomposition of MBN.



A standard of 1-naphthaisocyanate (I) was purchased from the Aldrich Chemical Company and analyzed by GC/MS. The mass spectrum of this standard was virtually identical with that of the unknown compound. However, their GC retention times were different by 0.2 min, suggesting that the unknown compound might be another isomer, but certainly not 1-naphthaisocyanate.

To further examine the structure of this component, the IR spectrum for this component was obtained by GC/FTIR. The absence of the absorption bands associated with -N=C=O stretching (near 2300 cm^{-1}) and with -C=N stretching (near 2200 cm^{-1}) immediately ruled out the possibility of compounds I or II as being the correct assignment for component 4. In fact, except for aromatic -C-H stretching at 3069 cm^{-1} , no absorption bands were observed in the spectral region between 3950 cm^{-1} and 1600 cm^{-1} , which suggested that the component possessed a condensed ring

FIGURE 3

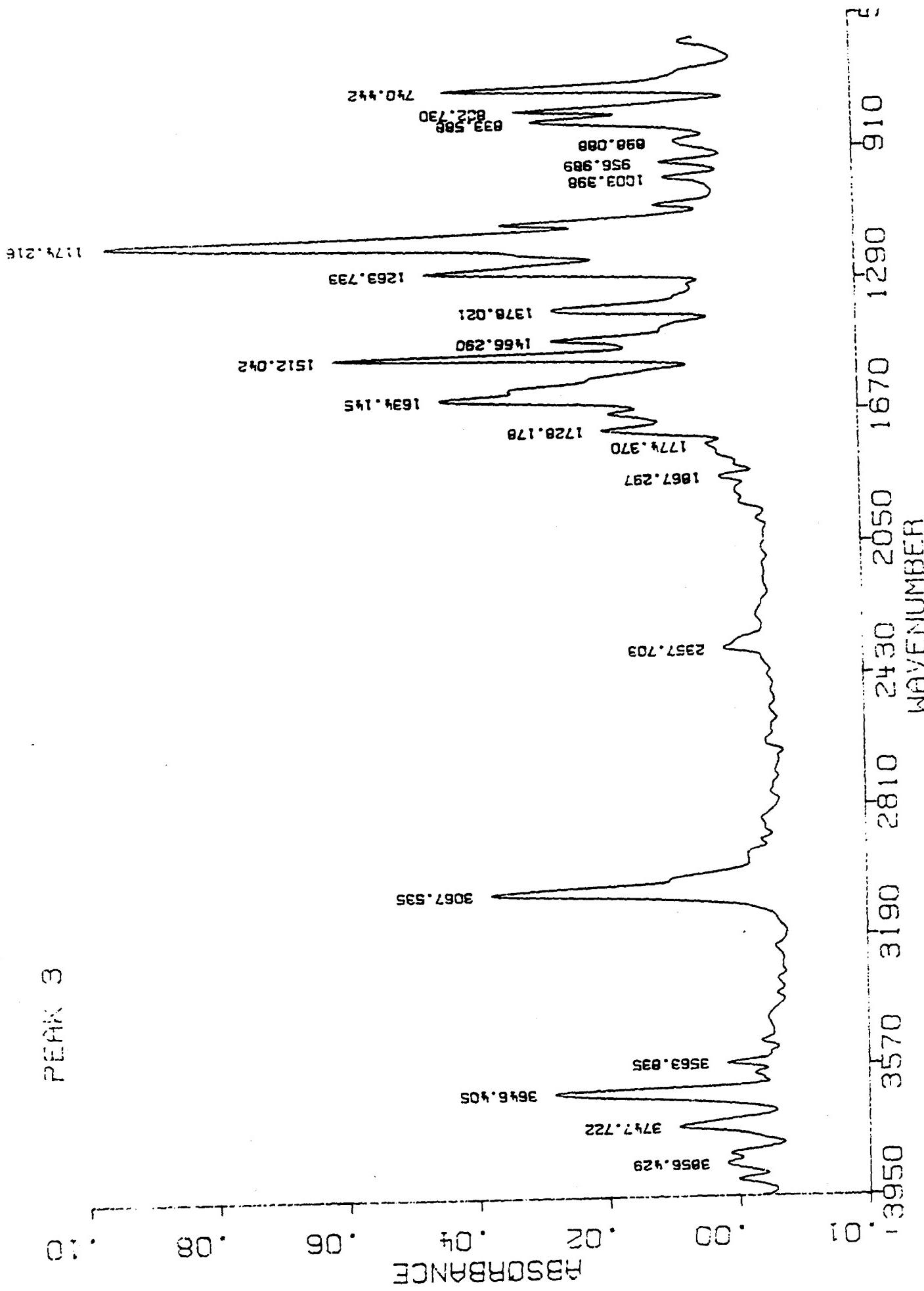
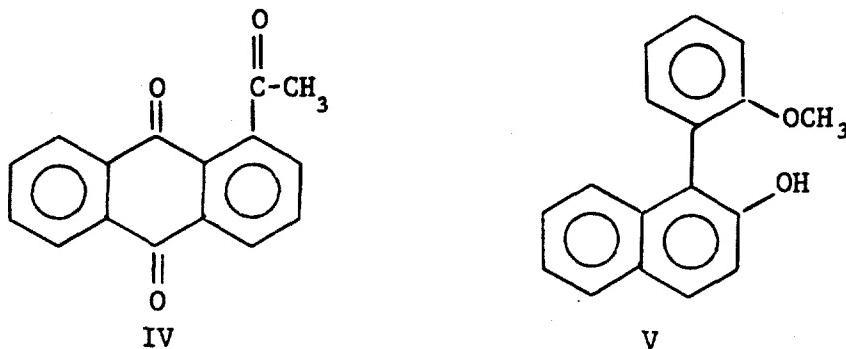


Figure D-2. IR Spectrum of 2-Naphthol Identified in Red Smoke Particulates by GC/FTIR

structure. Furthermore, the presence of -C=N stretching at 1574 cm^{-1} and asymmetrical ether -C-O-C- stretching at 1234 cm^{-1} correlated well with structure III. Therefore, this compound tentatively was assigned as structure III, i.e., naphtha-(1,2-d)-oxazole.

Similarly, three similar compounds were tentatively assigned as C₁, C₂, and C₃ homologues of naphtha-(1,2-d)-oxazole. These assignments were based primarily on the low resolution MS spectra obtained from each of these components and the IR spectrum obtained from the component assigned as the C₁ homologue. The following ions were observed for each of the homologues: C₁ (m/z = 183, 154, 140, 128, 114, and 88), C₂ (m/z = 197, 169, 141, 114, and 88), and C₃ (m/z = 211, 183, 169, 141, 114, and 88). In addition to -C=N stretching (1588 cm^{-1}) and -C-O-C- stretching (1221 cm^{-1}) bands an absorption band at 2946 cm^{-1} (alkyl -C-H stretching) was observed associated with the C₁ homologue.

Another compound which had previously been observed in the red particulates was also observed in the present study. The low resolution mass spectrum of this component exhibited a molecular ion at m/z 250 and fragment ions at m/z 235, 218, 189, 178, 152, and 94, and could be assigned as either aceytylanthraquinone (IV) or methoxyphenylnaphthal (V). LD/FTMS, however, showed that this compound had an elemental composition of C₁₇H₁₄O₂ (measured 250.108; calculated 250.099), which precluded the assignment as structure IV. Several infrared absorption bands were observed, at 3580 cm^{-1} (C-H stretch), 2947 and 2840 cm^{-1} (alkyl C-H stretch), 3069 cm^{-1} (aromatic C-H stretch), and 1260 cm^{-1} (aryl-alkyl ether stretch). This information led to the tentative assignment of this compound as methoxyphenylnaphthal (V), or a similar isomer.



In summary, the chemical composition of the particulates from the grenade from the third lot, which showed a "normal" production of red smoke, did not differ qualitatively from the smoke generated from the earlier studies (Figure D-3). Quantitatively, it appears that the major difference between this last grenade and the previously tested grenades is that although the amount of MBN has decreased substantially in the combusted particulates, the ratio of DMA to MBN is much lower than in the original smoke mix. Increases in decomposition products from MBN are observed, including 2-methoxyaniline, naphtha-(1,2-d)-oxazole, and methoxyphenylnaphthal (or a similar compound).

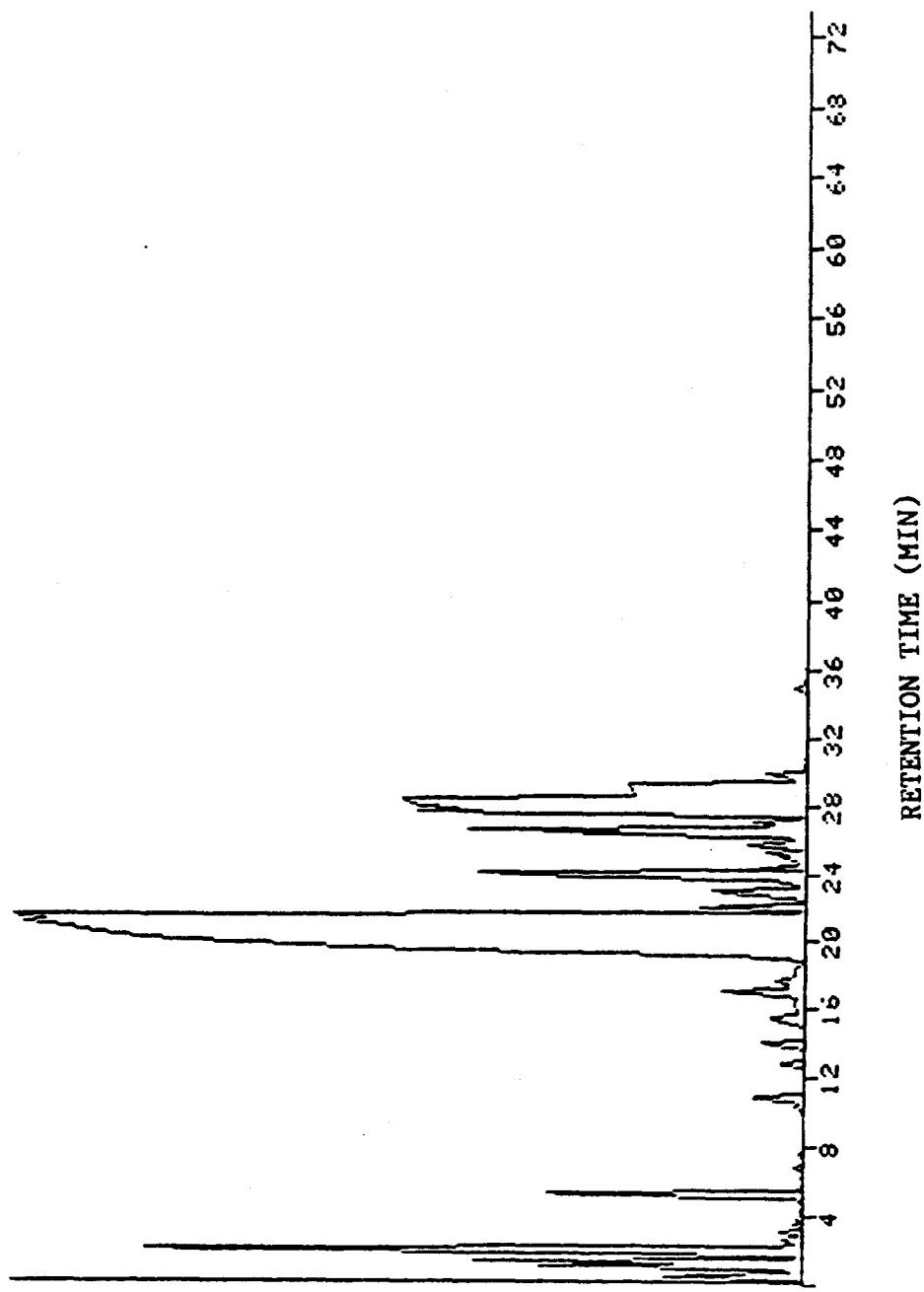


Figure D-3. Reconstructed GC/MS Chromatogram of Red Smoke Mix Vapor-Phase Trapped on Tenax

The volatile components from the red smoke generated from the third lot of grenades were trapped on Tenax resin and characterized as outlined previously in Appendix A. The tentatively identified compounds are listed in Table D-2. Differences are observed in the compounds identified from this red smoke and those observed in the previous "abnormal" smokes. Most significant is the apparent absence of major quantities of isocyanatobenzene (or cyanophenol or other C₆H₅NO isomer) and quinoline (or other C₉H₇N isomer) in the "normal" red smoke volatiles. Both of these compounds were thought to arise from MBN, and may account for the difference in the ratios of MBN to DMA in the red smoke particulates observed between the different grenade lots (see above). Methylphenol (or more likely, methoxybenzene) and methoxyaniline, would also arise from a decomposition of MBN, and are also major constituents in the volatile materials collected from the red smoke mix.

Table D-2. Volatile Components Collected on Tenax Traps
from the Combustion of Red Smoke Mix*

Benzene	C ₀ **, C ₁ , C ₂ , Cl, CN, CHO
Cyclohexane	C ₀
Styrene	C ₀ , C ₂
Phenylacetylene	C ₀ , C ₂
Phenol	C ₁ ** (or methoxybenzene)
Aniline	Cl, CH ₃ O**, C ₂ H ₅ O
Naphthalene	C ₀
Miscellaneous compounds	Acetone Chloroform C ₁ -furan C ₁ -benzoate Benzofuran

*Cn represents number (n) of alkyl carbon substituent on parent compound.

**Quantity greater than 5% of total chromatograph area, other components present at levels between 0.2 and 5%.

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